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ON THE BEHAVIOR OF IODINE AND BROMINE TOWARDS CHLORINE HEPTOXIDE AND PERCHLORIC ACID.

BY ARTHUR MICHAEL AND WALLACE T. CONN.

The first results indicating the property of iodine to replace chlorine in its oxygen acids, which is at present generally accepted as a fact, may be found in the investigation of Humphry Davy[1] on iodine, who discovered iodic acid by treating the element with chlorine monoxide, hypochlorous acid, or chlorine dioxide. Millon[2] subsequently found that iodine heated with aqueous potassium chlorate and a small quantity of nitric acid yields potassium iodate. In 1835 Balard[3] noticed that hypochlorous acid reacts with bromine to form bromic acid, but, contrary to his expectation, as the "electronegative tendency of bromine is much less than that of chlorine," he was unable to realize this synthesis by using chlorine dioxide, or a concentrated solution of chloric acid.

These reactions were considered to be oxidations, and the conception of a direct replacement of chlorine by iodine or bromine is based on the observations of H. Kaemmerer. According to this work the following reactions may be realized :

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[1] J. Phys. **77**, 456.

[2] Ann. chim. phys. [3], **9**, 400.

[3] J. prakt. Chem., **4**, 169.

I. Hot aqueous chloric acid and bromine give traces of bromic acid, which, however, is difficult to detect, as it is usually destroyed.[1]

II. Bromine reacts easily with the vapor of hydrated perchloric acid to form perbromic acid.[2]

III. A concentrated solution of perchloric acid heated with iodine gives periodic acid and chlorine.[3]

Evidence soon accumulated which went to show that some of the statements made by Kaemmerer in these researches are not trustworthy. J. Thomsen[4] proved that the heat of formation of aqueous bromic acid is considerably less than that of aqueous chloric acid, which fact made the formation of bromic acid from bromine and chloric acid difficult to understand, and, as a much more competent investigator than Kaemmerer, Balard, had previously examined this question and found that no reaction takes place, it may fairly be assumed that this synthesis of bromic acid has never been realized. Then MacIvor,[5] Muir,[6] and Wolfram[7] endeavored to obtain perbromic acid from perchloric acid and bromine, but without success. Indeed, the last chemist showed that the liquid obtained by repeating the work of Kaemmerer really gave the reactions stated as characteristic for perbromic acid, but it consisted of perchloric acid, mixed with some sulphuric acid, which Kaemmerer used in this experiment to generate the perchloric acid. As Kaemmerer published no quantitative work on the subject, and based the existence of perbromic acid solely on these qualitative tests, it is obvious that perbromic acid never has had a serious claim for existence. That it cannot be formed from perchloric acid, we have shown still more conclusively, inasmuch as we find that pure perchloric acid is without action on bromine, even by long exposure to sunlight, or on warming; nor does chlorine heptoxide react with the element. The direct replacement of chlorine in chloric and perchloric acids by iodine from a thermochemical point of view is more probable than by bromine, since Thomsen[1] showed that the heat of formation of the oxy-acids of iodine is considerably greater than that of the corresponding chlorine acids. The formation of iodic acid from iodine and chloric acid, or any of the less oxidized oxy-acids, is therefore simply a question of oxidation. It is, however, the formation of periodic acid from perchloric acid and iodine, which has been considered a complete proof of the capability of iodine to replace chlorine, as the direct oxidation of iodine has never led to a higher state of oxidation than iodic acid, although hypochlorous and chloric acids have been used, which are much stronger oxidizers than perchloric acid. We have repeated this work of Kaemmerer, using pure perchloric acid of different concentrations, and find that there is not even a trace of periodic acid formed in this reaction, which proceeds by the oxidation of iodine to iodic acid. An analogous result was obtained from chlorine heptoxide, which leads to the formation not of iodine heptoxide, but of the pentoxide.

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[1] Pogg. Ann., **138**, 400.

[2] J. prakt. Chem., **90**, 190; Pogg. Ann., **138**, 405.

[3] Pogg. Ann., **138**, 406.

[4] Ber. d. chem. Ges., **6**, 429.

[5] Chem. News, **33**, 35.

[6] J. Chem. Soc., **30**, 469.

[7] Ann. Chem. (Liebig), **198**, 95.

There is no reaction known which offers the slightest evidence that bromine or iodine is capable of directly replacing chlorine in its oxy-acids; indeed, from a theoretical point of view, such a procedure, implying as it does the direct substitution of an element joined to a number of oxygen atoms, is exceedingly improbable. The formation of bromic acid from aqueous hypochlorous acid and bromine, whereas aqueous chloric acid is without action, is due to the tendency of hypochlorous acid to pass over into chloric acid; a conversion which may be assumed to take place through the decomposition of water:

$$\begin{aligned}
&HOCl + H_2O = HOClO + H_2;\\
&HOCl + H_2 = HCl + H_2O;\\
&HOClO + H_2O = HOClO_2 + H_2;\\
&HOCl + H_2 = HCl + H_2O.
\end{aligned}$$

The presence of bromine can only have the effect of favoring the decomposition of water, with the formation of hydrobromic acid, and this acid reacting with hypochlorous acid

[1] Ber. d. chem. Ges., 6, 429.

yields chloride of bromine, which, in the presence of water and chlorine, formed by the interaction of hypochlorous and hydrochloric acids, is converted into bromic acid. As chloric acid does not pass over into perchloric acid nearly as easily as hypochlorous does into chloric acid, the failure of the first acid to induce the indirect oxidation of bromine will be readily understood.

Another reaction, which seems to imply the replacement of chlorine by bromine or iodine, is the formation of bromic or iodic acid by the action of bromine or iodine on aqueous sodium chlorate, and we are indebted to Potilitzin[1] for the correct interpretation of these changes. This chemist proved that chlorine reacts with sodium bromate, and bromine with sodium chlorate, although much less readily in the last instance, according to the equations:

$$5NaBrO_3 + 3Cl_2 + 3H_2O = 5NaCl + 5HBrO_3 + HClO_3.$$
$$5NaClO_3 + 3Br_2 + 3H_2O = 5NaBr + 5HClO_3 + HBrO_3.$$

Potilitzin particularly emphasizes the fact that these decompositions do not proceed by direct substitution of the halogens. It is obvious that the formation of bromic acid from sodium chlorate is due to the greater affinity of sodium for bromine than for $—OClO_2$; this causes the decomposition, with the intervention of water, and formation of hypobromous acid, which is oxidized to bromic acid. The reaction is essentially of the same character as the formation of sodium bromate from bromine and caustic soda, only it proceeds much less readily, as sodium chlorate represents a much better neutralized sodium derivative than the alkali.

In the preparation of chlorine heptoxide we have found that the danger of explosion may be decidedly reduced by several slight modifications of our former directions.[2] In the first place, it is advisable, especially during warm weather, to keep the retort containing the phosphorus pentoxide at a lower temperature than —10° C., during the addition of perchloric acid, and for some hours afterwards. Instead of heating the retort gradually to 85° C. in a water-bath, it is better to heat slowly, and after two hours remove the heptoxide from the receiver, when about two-thirds of the amount formed has passed over; then four hours longer, at the same temperature, and finally to 85° C., when the last traces of heptoxide are driven off.

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[1] Ber. d. chem. Ges., **20**^{III}, 777.

[2] This JOURNAL, **23**, 445.

Iodine and chlorine heptoxide usually react in the cold, and if the substances are in a sealed tube a dangerous explosion will probably ensue, which may be avoided to a considerable extent by adhering to the following directions: Pure and finely powdered iodine is brought into a tube sealed at one end, of a diameter of about an inch and a half, and the open end drawn out so as to admit the almost capillary stem of a funnel. The tube is then placed in a freezing mixture and the freshly prepared chlorine heptoxide introduced, in the proportion of an atom of iodine to a molecule of the heptoxide. At this stage of the operation there seems to be but little danger of an explosion, but it is well to seal the tube at once and place it, kept in the freezing-mixture, in a dark closet, where no damage will be done by an explosion. A very energetic action soon takes place, with the liberation of heat, and formation of a white solid. After standing twelve hours about two-thirds of the iodine has been converted into the white compound, and the tube, after opening the sealed end to allow the greenish gas that has been formed to escape, and resealing, is put in a bottle of water and exposed to bright sunlight until the iodine has completely disappeared. This takes from two days to a week. It is well to open the pointed end of the tube several times, as the danger of explosion is thereby materially lessened.

The contents of the tube consisted of a whitish powder, which fumed in the air. When heated to 100° C. in a vacuum, an oily liquid came off, which, taken up in water, gave reactions for perchloric acid, and the solid residue gave all the tests for iodine pentoxide. A portion was dissolved in water, precipitated by silver nitrate, and the silver salt dried to constant weight:

0.4791 gram salt gave 0.3987 gram AgI.

	Theory for $AgIO_3$.	Found.
AgI	83.03	83.22

The action of anhydrous perchloric acid on iodine is much less energetic than that of chlorine heptoxide, and the experiment may be done as described with the heptoxide without danger of explosion. The iodine (0.5 atom of the element to 1 molecule acid) dissolved in the acid, and, after keeping the tube for a day in a dark place, it was exposed to bright sunlight. Oxidation soon began, even in the dark, but it required, at winter temperature, several weeks before the iodine had disappeared, unless the tube was exposed to sunlight, when the oxidation proceeded more rapidly. The product is a moist, pinkish, crystalline powder. It was heated in a vacuum, when a yellowish body remained, consisting of small homogeneous needles. This substance is extremely hygroscopic and rapidly turns black on exposure to the air, owing to the liberation of iodine. When the substance is heated, iodine is given off and a white residue remains, which, as it is converted into iodic acid by dissolving in water, evidently consists of iodine pentoxide. In contact with water it is immediately decomposed with the liberation of iodine and formation of iodic acid.

0.2042 gram substance, dried to constant weight at 70° C. in a vacuum, gave 0.1670 gram free iodine when treated with water.

	Theory for HI_7O_3.	Found.
I_6	81.2	81.7

This substance is interesting from several points of view. In the first place, it is formed in the presence of a considerable excess of perchloric acid, with long exposure to sunlight, and, nevertheless, represents the final stage of the oxidation of iodine, under these conditions. It would further seem to prove that the molecule of solid iodine contains a far greater number of atoms than two, and its slow oxidation causes only a partial breakdown of this large molecule. This behavior of iodine towards slow and rapid oxidation is comparable to the action of chlorine and that of the less energetic iodine on the tetratomic phosphorus molecule, inasmuch as by the last reaction a phosphorus derivative containing two atoms of the element in its molecule may be obtained.[1]

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[1] There is no direct proof of the presence of hydrogen in this compound, and it may consist only of iodine and oxygen. The above study of the behavior of iodine

Kaemmerer,[1] in his supposed conversion of perchloric into periodic acid, heated a concentrated solution of the first acid with iodine. We tried to repeat this experiment by heating iodine with a pure and concentrated perchloric acid (1.57 sp. gr.) in a flask, whose long neck was enclosed as a condenser. After heating a short time a reaction took place, and the oxidation was then soon completed. The white crystalline substance was filtered under pressure, washed with a little water, then recrystallized, and proved to be iodic acid. An analysis of the silver salt gave the following result :

0.4679 gram dry silver salt gave 0.3916 gram AgI.

	Theory for $AgIO_3$.	Found.
AgI	83.03	83.61

We then varied the experiment by taking perchloric acid of different strengths, and the conditions of temperature, but in all cases a similar result was obtained ; that is, iodic acid was formed. We were also unable to detect the presence of periodic acid in the mother-liquors from the iodic acid, and we do not hesitate to state that the formation of periodic from perchloric acid, as described by Kaemmerer, is incorrect.

Bromine and chlorine heptoxide may be exposed for weeks in a sealed tube to sunlight without any reaction taking place, even in presence of a very large excess of oxide. Nor did we notice an action between anhydrous perchloric acid and bromine, when they were exposed, in a sealed tube, for a long time to sunlight, or on warming the tube. We were equally unable to oxidize bromine by boiling it a long time with a concentrated solution of perchloric acid.

It is not easy to understand the confidence which is still placed in the above investigations of Kaemmerer, as a very considerable portion of the work has been experimentally disproved, and its character, mostly mere statements, unaccompanied by any

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towards perchloric acid is preliminary, and the substance will be more fully analyzed and examined. Several oxides of iodine—$I_{10}O_{19}$ and I_8O_{18}— containing a number of iodine atoms to the molecule, and obtained by moderate oxidation of the element—have been previously described, but their existence is now considered doubtful. In view of the important theoretical bearing of the subject, the behavior of iodine, as well as that of some other elements, towards the slow action of perchloric and nitric acids and other oxidizers will be studied.

[1] Pogg. Ann., 138, 406.

quantitative evidence, hardly seemed to have invited it. It is to be hoped, however, that such gross errors as the existence of perbromic acid, or the direct substitution of chlorine or bromine in their oxy-acids by iodine, which find a place in most text-books, even though of very elementary character, will soon be consigned to the oblivion, which they have long merited.

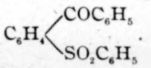
TUFTS COLLEGE, MASS.

ORTHOPHENYLSULPHONEBENZOIC ACID AND RELATED COMPOUNDS.[1]

BY HALL CANTER.

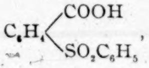
Introduction.

Working in this laboratory Newell[2] undertook an investigation, the primary object of which was to make and study orthobenzoyldiphenylsulphone,



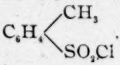
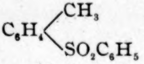
$$C_6H_4\Big\langle\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}.$$

He commenced his work in the para series and met with results so satisfactory as to cause him to confine his work to that series. The research recorded in these pages was begun with the intention of preparing and studying orthophenylsulphonebenzoic acid,



$$C_6H_4\Big\langle\begin{matrix}COOH\\SO_2C_6H_5\end{matrix},$$

and compounds derived from it.

The substance that served as a starting-point in the work was orthotoluenesulphone chloride,  $C_6H_4\Big\langle\begin{matrix}CH_3\\SO_2Cl\end{matrix}$. By subjecting this to the Friedel-Crafts reaction, employing benzene and aluminium chloride, it was thought possible to pass to orthotolylphenylsulphone,  $C_6H_4\left\langle\begin{matrix}CH_3\\ SO_2C_6H_5\end{matrix}\right.$; then by means of a suitable oxidizing agent to transform the methyl group into carboxyl and obtain orthophenylsulphonebenzoic acid,

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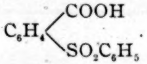
[1] From the author's dissertation submitted to the Board of University Studies of the Johns Hopkins University, June, 1900, for the degree of Doctor of Philosophy.

[2] This JOURNAL, **20**, 302.

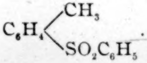


$$C_6H_4\left\langle\begin{matrix}COOH\\ SO_2C_6H_5\end{matrix}\right. .$$

Preparation of Material.

The orthotoluenesulphone chloride employed was a kilogram presented to Professor Remsen by the chemical factory of von Heyden.[1] This was filtered from a small quantity of solid material contained in it, and then used. The benzene was redistilled and thoroughly dried. The chloride of aluminium was the fresh commercial article obtained from the laboratory.

Orthotolylphenylsulphone,



$$C_6H_4\left\langle\begin{matrix}CH_3\\ SO_2C_6H_5\end{matrix}\right. .$$

The isomeric paratolylphenylsulphone has been prepared by several methods, among others that of Beckurts and Otto,[2] who employed toluene, aluminium chloride, and benzenesulphone chloride. A method perfectly analogous to this, and the same as that employed by Newell,[3] was made use of in preparing orthotolylphenylsulphone. The following directions were found to be satisfactory :

For each 25 gram portion of orthotoluenesulphone chloride 100 grams of benzene and 30 grams of aluminium chloride were used. The amount of toluenesulphone chloride employed was varied up to 40 grams, the proportion of benzene and aluminium chloride being the same. Though the reaction progressed apparently well, yet the yield of orthotolylphenylsulphone was not proportionately increased, and the sulphone chloride was always used in portions of 25 grams. Orthotoluenesulphone chloride easily dissolves in benzene at a slightly elevated temperature, forming a solution of dark wine color. Aluminium chloride is added in 8 or 10 portions during an hour. Upon addition of the first portion reaction begins, and gradually becomes more energetic. A temperature of 75° causes the reaction to proceed smoothly, yet rapidly, so the flask containing the mixture was kept in a water-bath at this temperature. When three-fourths of the aluminium chloride has been added, reaction becomes less violent with each subsequent addition; and when all the aluminium chloride has been added, the temperature of the water-bath is kept at 80° to 85° till the evolution of hydrochloric acid ceases. The liquid in the flask at this stage has become darker, and is now poured into a large beaker containing tepid water to which a little hydrochloric acid has been added. The liquid must be added slowly to the water and stirred constantly; otherwise sufficient heat is generated by the action of water on undecomposed aluminium chloride to cause partial evaporation of the benzene—a thing not desirable at this stage. On top of the water appears the layer of benzene containing the product of the reaction in solution. This is separated, passed through a filter, again washed with water to remove any chloride of aluminium, and then dried. Most of the benzene is distilled off, and the remaining portion is evaporated from a beaker on the water-bath. The crude sulphone solidifies, showing a crystalline structure, and this hardening can be quickened by stirring with a glass rod. The hardened, dark-brown mass is dissolved in 95 per cent alcohol and filtered from a small quantity of insoluble matter. To remove the color the solution in alcohol is boiled several times with animal charcoal. A considerable amount of the sulphone remains behind with the charcoal, and several treatments with boiling alcohol are necessary to recover all of it. Orthotolylphenylsulphone crystallizes in white leaflets that melt at 67°.5 to 68° (uncorr.). It is easily soluble in petroleum ether, ordinary ether, benzene, alcohol, glacial acetic acid, and to a very slight degree in water. It is dissolved by strong nitric acid, from which it can be recovered by adding water; insoluble in hydrochloric acid. Upon analysis the following results were obtained:

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[1] I beg here to express my hearty thanks to the officers of the von Heyden factory for their liberality in furnishing the material, and for other courtesies.—I. R.

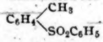
[2] Ber. d. chem. Ges., **11**, 2068.

[3] *Loc. cit.*

I. 0.1831 gram substance gave 0.4488 gram CO_2 and 0.0877 gram H_2O.

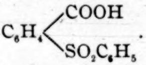
II. 0.2207 gram substance gave 0.5423 gram CO_2 and 0.1063 gram H_2O.

III. 0.1333 gram substance gave 0.1349 gram $BaSO_4$.

	Calculated for  $C_6H_4\langle{}^{CH_3}_{SO_2C_6H_5}$	Found. I.	II.
C	67.24	66.85	67.01
H	5.18	3.33	5.35
S	13.81	13.91	....

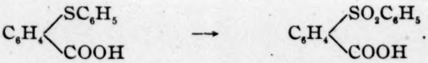
The determinations of carbon and hydrogen were made by the lead chromate method of de Roode, and the sulphur by the method of Carius.

Orthophenylsulphonebenzoic Acid,



$$C_6H_4\langle{}^{COOH}_{SO_2C_6H_5}.$$

Graebe and Schulteiss[1] claim to have made this acid in 1891. In the course of an investigation carried out by them they treated phenylthiosalicylic acid with strong nitric acid. The reaction-product, when brought into water, formed an oil, which solidified upon standing. Purified by ether and crystallized from 90 per cent alcohol, their new acid appeared in the form of white needles, containing 1 molecule of water of crystallization and melting at 99°. When heated to 105° this water is lost and the acid then melts at 152°. They called the substance sulphobenzidorthocarbonic acid. The relation to phenylthiosalicylic acid is seen thus:



$$C_6H_4\langle{}^{SC_6H_5}_{COOH} \longrightarrow C_6H_4\langle{}^{SO_2C_6H_5}_{COOH}.$$

In this investigation orthotolylphenylsulphone was subjected to the action of oxidizing agents. In the first instance chromic acid was tried. A small quantity of the sulphone was dissolved in glacial acetic acid in a flask attached to a return-condenser, and to this solution was added chromic acid in glacial acetic acid. The flask was then heated a sufficiently long time and the product examined. This method was abandoned, as a relatively small amount of acid was thus obtained. Potassium permanganate was used as the oxidizing agent and the process in detail was as follows:

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[1] Ann. Chem. (Liebig), 263, 7.

Ten grams of orthotolylphenylsulphone were suspended and partially dissolved in 2.5 liters of boiling water. Into the flask, steam was continuously conducted to prevent bumping and to keep the water hot. Finely powdered potassium permanganate in quantity slightly in excess of the calculated amount was added in small spoonfuls throughout the space of an hour and a half. The boiling was continued for fifteen hours, till the contents of the flask became quite black, and a small portion removed and filtered appeared quite clear. A few cubic centimeters of alcohol were added, the liquid was filtered from the manganese dioxide and evaporated to the volume of 1 liter. Upon addition of hydrochloric acid the acid was precipitated as a white flocculent mass. If precipitated from a cold solution it shows more of a crystalline structure. The acid was crystallized from alcohol, but it was hardly possible to obtain it pure in this way, because of the presence of some unchanged sulphone. The barium salt of the acid was made, but even this carried with it some sulphone. The solution of the barium salt was then evaporated to dryness, and the dry salt was treated several times with boiling alcohol. In this manner the remaining small portions of the sulphone were removed. The remaining barium salt was recrystallized, and from this the free acid was obtained. This was purified by recrystallization from ordinary alcohol.

Orthophenylsulphonebenzoic acid crystallizes in clear small plates, frequently grouped in clusters. It is insoluble in water and readily soluble in alcohol. A portion heated for an hour and a half in an air-bath, at a temperature of 130°, lost nothing in weight. The acid, as above obtained, melts at 267° to 268° (uncorr.).

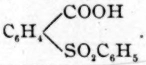
Analysis:

0.2064 gram substance gave 0.4480 gram CO_2 and 0.07709 gram H_2O.

0.2625 gram substance gave 0.2346 gram $BaSO_4$.

	Calculated for $C_6H_4<^{COOH}_{SO_2C_6H_5}$.	Found.
C	59.54	59.20
H	3.82	4.15
S	12.21	12.28

Salts of Orthophenylsulphonebenzoic Acid,



$$C_6H_4<^{COOH}_{SO_2C_6H_5}.$$

In addition to the analysis of the acid several salts were made, the analysis of which confirms the structure above assigned the acid.

Barium Salt.—The salt is readily soluble in water and crystallizes from moderately concentrated solutions in clear, white needles, some being 15 mm. in length. If the solution is too concentrated the salt appears in the form of granular nodules. Upon analysis the following results were obtained :

0.1560 gram salt, heated to 160° for an hour, lost 0.0118 gram H_2O.

0.1560 gram salt gave 0.0507 gram $BaSO_4$.

0.1972 gram salt at 160° lost 0.0151 gram H_2O.

0.1972 gram salt gave 0.0639 gram $BaSO_4$.

	Calculated for	Found.	
	$\left(C_6H_4<^{COO}_{SO_2C_6H_5}\right)_2Ba.3H_2O$.	I.	II.
H_2O	7.57	7.56	7.65

	Calculated for	Found.	
	$\left(C_6H_4<^{COO}_{SO_2C_6H_5}\right)_2Ba$.	I.	II.
Ba	20.81	20.68	20.64

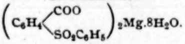
Magnesium Salt.—This salt was made by adding to a solution of the barium salt a solution of pure magnesium sulphate in quantity just sufficient to precipitate the barium present. The salt is easily soluble in water and crystallizes from it in the form of short, silken needles, which show a tendency to arrange themselves in clusters. Results of analyses were as follows :

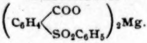
0.1827 gram salt lost 0.0383 gram H_2O below 160°.

0.1827 gram salt gave 0.0320 gram $MgSO_4$.
0.1618 gram salt lost 0.0339 gram H_2O below 160°.
0.1618 gram salt gave 0.0293 gram $MgSO_4$.

A third determination of water of crystallization was made with some of the same salt that had been dried between filter-paper for several days.

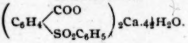
0.1038 gram salt lost 0.0215 gram H_2O below 160°.

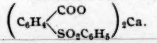
	Calculated for	Found.		
	 $\left(C_6H_4\begin{smallmatrix}COO\\SO_2C_6H_5\end{smallmatrix}\right)_2Mg.8H_2O.$	I.	II.	III.
H_2O	20.86	20.96	20.95	20.71

	Calculated for	Found.	
	 $\left(C_6H_4\begin{smallmatrix}COO\\SO_2C_6H_5\end{smallmatrix}\right)_2Mg.$	I.	II.
Mg	4.39	4.40	4.55

Calcium Salt.—This is very easily soluble in water and crystallizes from it in short needles, almost wholly grouped in clusters. Upon analysis the following results were obtained:

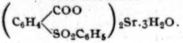
0.1595 gram salt lost 0.0206 gram H_2O below 160°.
0.1595 gram salt gave 0.0333 gram $CaSO_4$.
0.1452 gram salt lost 0.0186 gram H_2O below 160°.
0.1452 gram salt gave 0.0306 gram $CaSO_4$.

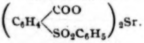
	Calculated for	Found.	
	 $\left(C_6H_4\begin{smallmatrix}COO\\SO_2C_6H_5\end{smallmatrix}\right)_2Ca.4\frac{1}{2}H_2O.$	I.	II.
H_2O	12.62	12.91	12.81

	Calculated for	Found.	
	 $\left(C_6H_4\begin{smallmatrix}COO\\SO_2C_6H_5\end{smallmatrix}\right)_2Ca.$	I.	II.
Ca	7.11	7.05	7.10

Strontium Salt.—This salt is easily soluble in water and crystallizes in small leaflets or flakes. Analysis resulted as follows:

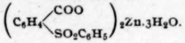
0.1789 gram salt lost 0.0143 gram H_2O below 160°.
0.1789 gram salt gave 0.0494 gram $SrSO_4$.
0.1232 gram salt lost 0.0099 gram H_2O.
0.1232 gram salt gave 0.0343 gram $SrSO_4$.

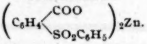
	Calculated for	Found.	
	 $\left(C_6H_4\genfrac{}{}{0pt}{}{COO}{SO_2C_6H_5}\right)_2Sr.3H_2O.$	I.	II.
H_2O	8.13	7.99	8.03

	Calculated for	Found.	
	 $\left(C_6H_4\genfrac{}{}{0pt}{}{COO}{SO_2C_6H_5}\right)_2Sr.$	I.	II.
Sr	14.35	14.28	14.47

Zinc Salt.—To the acid suspended in water an excess of pure zinc oxide was added. The flask containing the substance was attached to a return-condenser, and the contents heated to boiling for two hours. After standing in dilute solution over night, a few crystals of the salt appeared in the form of short, glistening needles; but to procure the salt in quantity sufficient for analysis, the solution was evaporated to a small volume.

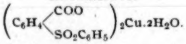
0.1678 gram salt lost 0.0138 gram H_2O.
0.1678 gram salt gave 0.0418 gram $ZnSO_4$.
0.1592 gram salt lost 0.0132 gram H_2O.
0.1592 gram salt gave 0.0398 gram $ZnSO_4$.

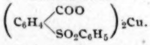
	Calculated for	Found.	
	 $\left(C_6H_4\genfrac{}{}{0pt}{}{COO}{SO_2C_6H_5}\right)_2Zn.3H_2O.$	I.	II.
H_2O	8.42	8.22	8.29

	Calculated for	Found.	
	 $\left(C_6H_4\genfrac{}{}{0pt}{}{COO}{SO_2C_6H_5}\right)_2Zn.$	I.	II.
Zn	11.11	10.97	11.15

Copper Salt.—In a flask attached to a condenser the free acid and the copper oxide were boiled together and the solution of the copper salt filtered off. Immediately upon cooling some of the salt separated out from the dilute solution, but during the night there was no increase in amount, and the solution was evaporated in stages till the salt crystallized more abundantly. It is not easily soluble in water, and crystallizes either in small plates or in the form of a powder. The salt is dark-green in color, and after losing its water of crystallization it turns light-blue. Trouble was had in the first trials to determine the amount of water contained, as the salt decomposes below 160°. Analysis resulted as follows:

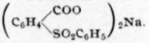
0.1488 gram salt lost 0.009 gram H_2O.
0.1488 gram salt gave 0.0186 gram CuO.

	Calculated for  $\left(C_6H_4<\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Cu.2H_2O$.	Found.
H_2O	5.79	6.04

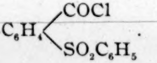
	Calculated for  $\left(C_6H_4<\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Cu$.	Found.
Cu	10.81	10.62

Sodium Salt.—This salt was prepared from the barium salt, instead of employing the free acid and sodium carbonate. To a solution of the barium salt a dilute solution of sodium sulphate is slowly added till all the barium present is just precipitated. The salt is exceedingly easily soluble in water. After standing more than two months in a desiccator it crystallized from a syrupy solution in fine silken needles. Shaking the beaker causes them partially to dissolve. The following analyses were made of the dry amorphous salt:

0.1409 gram salt gave 0.0357 gram Na_2SO_4.
0.1521 gram salt gave 0.0375 gram Na_2SO_4.

	Calculated for  $\left(C_6H_4<\begin{matrix}COO\\SO_2C_6H_5\end{matrix}\right)_2Na$.	Found. I.	II.
Na	8.09	8.21	7.98

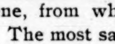
Orthophenylsulphonebenzoyl Chloride,



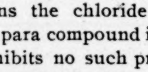
$$C_6H_4<\begin{matrix}COCl\\SO_2C_6H_5\end{matrix}.$$

This compound can be made either by treating a salt of orthophenylsulphonebenzoic acid, preferably the sodium salt, with phosphorus pentachloride, or by treating the free acid with the same reagent. The latter method was employed. A quantity of the acid was mixed with a slight excess of pentachloride of phosphorus in an evaporating dish, and the two were rubbed together with a pestle. At ordinary temperature the substances react slightly, and when heated to 45° on the water-bath the reaction proceeds rapidly, the whole mass becoming semi-liquid, or else granular, in structure. The dish was then placed in a sulphuric-acid bath and heated for two hours at a temperature of 200°. In this way most of the oxychloride of phosphorus was expelled, while a slight evolution of hydrochloric acid was noticed so long as the heating was continued. Upon cooling, the substance solidifies to a dark-gray mass. Tepid water was added, the solid mass powdered into granular form, washed several times with cold water by shaking, and finally treated several times with water upon the filter-pump, and then dried between filter-paper. Orthophenylsulphonebenzoyl chloride is very difficultly soluble in boiling petroleum ether of 105° to 130°; difficultly soluble in absolute ether, from which it crystallizes in small, thin, clear plates; more readily, though not easily, soluble in boiling benzene, from which, upon evaporation, it crystallizes in plates. The most satisfactory solvent is glacial acetic acid, in which the chloride is easily soluble. From this it crystallizes in short needles arranged in clusters. After repeated crystallizations the chloride melted at 262°.5 to 263°.5. The isomeric para compound is slightly volatile, but the ortho chloride exhibits no such property. Some of the substance—0.1120 gram—that had been thoroughly dried and kept in a glass bottle, was heated gradually as high as 145°, but there was no loss in weight. A small quantity of the chloride was placed in a flask with cold water and shaken repeatedly. After standing for twenty-four hours there was slight decomposition, as indicated by silver nitrate. When boiled with water the chloride is quickly decomposed. A determination of chlorine in this way resulted as follows:

0.1756 gram chloride gave 0.8833 gram AgCl.

	Calculated for  $C_6H_4\left\langle\begin{array}{l}COCl\\SO_2C_6H_5\end{array}\right.$	Found.
Cl	12.62	12.45

Orthophenylsulphonebenzamide,

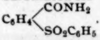


$C_6H_4\left\langle\begin{array}{l}CONH_2\\SO_2C_6H_5\end{array}\right.$.

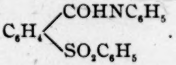
Pure orthophenylsulphonebenzoyl chloride was placed in a suitable flask and covered with strong ammonia. The vessel was kept at ordinary temperature, and vigorously shaken at intervals throughout twenty-four hours. There was no change apparent at the end of this time, except that some of the substance seemed to have passed into solution. The vessel was then placed in a water-bath, slightly evaporated, and allowed to stand over night, when the reaction-product appeared as a light crystalline powder. It is easily soluble in alcohol, and from this solution crystallizes in beautifully, regular, transparent plates. When the determination of the melting-point was made, the substance melted through a range of several degrees. After numerous crystallizations the same thing occurred, the melting beginning at about 220° and continuing up to 257°. At the same time a deposit was noticed on the glass in the upper part of the melting-point tube, evidently the sublimed amide. Another portion of the substance was then placed in a tube and both ends were sealed. Heated in an acid-bath the substance then melted at 245° to 255°. Analysis for nitrogen was made by the absolute method of Dumas, and the sulphur was determined by Liebig's method.

0.1844 gram amide gave 8.4 cc. = 0.0097 gram N under standard conditions.

0.1528 gram amide gave 0.1388 gram $BaSO_4$.

	Calculated for  $C_6H_4\left\langle\begin{matrix}CONH_2\\SO_2C_6H_5\end{matrix}\right.$.	Found.
N	5.37	5.26
S	12.27	12.48

Orthophenylsulphonebenzanilide,



$$C_6H_4\left\langle\begin{matrix}COHNC_6H_5\\SO_2C_6H_5\end{matrix}\right. .$$

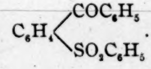
Some of this compound was made in two ways: Orthophenylsulphonebenzoyl chloride was dissolved in benzene and aniline was added in small portions, with continued shaking of the flask. Water was added to dissolve the aniline hydrochloride, and the anilide was subsequently purified. The following method was employed in making the anilide in quantity: An emulsion of aniline and water was made by vigorously shaking the two, aniline being employed in quantity representing 2 molecules for each one of the chloride to be used. Orthophenylsulphonebenzoyl chloride was finely powdered and added in small portions to the emulsion, the flask being shaken after each addition. Reaction takes place when the first portion of the chloride has been added, a grayish-brown, gummy substance appearing upon the surface of the liquid. The flask was shaken at intervals through two days, after which the anilide appeared as a finely divided, granular mass at the bottom of the vessel. This was filtered off and washed several times with dilute hydrochloric acid and then with water. It was dissolved in 95 per cent alcohol and treated twice with animal charcoal, but the solution always remained slightly colored. From alcohol the anilide crystallizes readily in small glistening plates, which melt at 234° to 235° (uncorr.). The estimations of nitrogen and sulphur were made as in the case of the amide, and gave the following results:

0.3122 gram anilide gave 10.8 cc. = 0.01238 gram N under standard conditions.

0.1602 gram anilide gave 0.1119 gram $BaSO_4$.

	Calculated for $C_6H_4\langle^{COHNC_6H_5}_{SO_2C_6H_5}$.	Found.
N	4.16	3.96
S	9.48	9.59

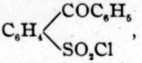
Orthobenzoyldiphenylsulphone,

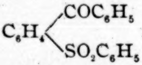
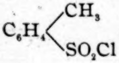
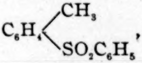
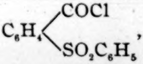
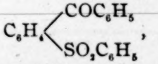


$$C_6H_4\langle^{COC_6H_5}_{SO_2C_6H_5}.$$

This compound was made in this laboratory by Remsen and Saunders,[1] who were working upon the chlorides of orthosulphobenzoic acid. By treating a mixture of these chlorides with benzene and aluminium chloride they obtained in the first instance a compound of the supposed structure

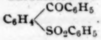
[1] This JOURNAL, **17**, 362.


$C_6H_4\left\langle\begin{matrix}COC_6H_5\\SO_2Cl\end{matrix}\right.$,

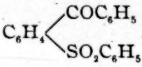
which they called orthobenzoylbenzenesulphone chloride. They obtained the same compound by treating the solid chloride of orthosulphobenzoic acid with benzene and aluminium chloride. By continued treatment of the mixed chlorides, as above, the intermediate substance first formed passes over to  $C_6H_4\left\langle\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}\right.$. To see whether or not the benzoyldiphenylsulphone above formed possesses the structure assigned to it, the method of making it in this investigation was brought into account. Starting with orthotoluenesulphone chloride,  $C_6H_4\left\langle\begin{matrix}CH_3\\SO_2Cl\end{matrix}\right.$, introducing the phenyl group,  $C_6H_4\left\langle\begin{matrix}CH_3\\SO_2C_6H_5\end{matrix}\right.$, oxidizing and then passing to the chloride,  $C_6H_4\left\langle\begin{matrix}COCl\\SO_2C_6H_5\end{matrix}\right.$, and then introducing another phenyl group,  $C_6H_4\left\langle\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}\right.$, there seems only one possible structure for orthobenzoyldiphenylsulphone. Its method of formation was as follows: Ten grams of orthophenylsulphonebenzoyl chloride were dissolved in benzene in a tubulated retort attached to a return-condenser. At ordinary temperature reaction did not take place upon the addition of aluminium chloride, and the water-bath in which the retort was placed was raised to 65°. After one-half hour the solution turned dark-red. When all the chloride of aluminium—12 grams—had been added, the contents of the vessel became quite dark, and the temperature was kept at 80° till hydrochloric acid ceased to be evolved. The introduction of the second phenyl group into the chloride seemed harder to accomplish than that of the first. When thereaction was completed the retort was slowly emptied into a large beaker of water, to which a little hydrochloric acid had been added. Considerable heat was generated, the water became milky, and the benzene arose to the surface, forming a dark-colored layer upon the water. This was separated, and the water treated several times with benzene. All the benzene was then filtered, thoroughly washed, and dried. Upon standing over night some crystals separated from the dilute solution. These were dissolved; most of the benzene was distilled off, and the remainder evaporated upon a water-bath, leaving the new compound in the form of a dark-brown crystalline substance. This was dissolved in alcohol, animal charcoal was added, and the solution was heated to boiling for several minutes. From the filtered solution orthobenzoyldiphenylsulphone quickly crystallizes in thin plates or leaflets, being difficultly soluble in alcohol. It is more easily soluble in benzene, from which it crystallizes in flakes, as in the first instance. The purified substance melted at 183° to 184°. The crystals are stable in the air ; they are not readily acted on by alcoholic potash ; they can be dissolved in warm, strong, nitric acid, and again recovered by addition of water ; strong hydrochloric acid has no effect upon them. Analysis for carbon and hydrogen by de Roode's method, and for sulphur by the method of Liebig gave the following results :

0.1660 gram substance gave 0.4288 gram CO_2 and 0.0658 gram H_2O.

0.1511 gram substance gave 0.1047 gram $BaSO_4$.

	Calculated for  $C_6H_4<\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}$	Found.
C	70.78	70.45
H	4.35	4.40
S	9.95	9.52

Orthobenzoyldiphenylsulphone was fused with an excess of potassium hydroxide, the heat being gradually intensified. When the substance begins to melt, some volatile substance escapes, and this fact probably accounts for the low determination in the case of the sulphur. Gradually the melting continues till the benzoyldiphenylsulphone forms with the molten potassium hydroxide a tranquil, dark straw-colored liquid, and this cools to a yellow-brown mass. When treated once or twice with hot water this partially dissolves, leaving a small insoluble residue behind. The filtered water solution, when treated with hydrochloric acid, gave a precipitate of benzoic acid, as determined by the melting-point. An accident caused the loss of the insoluble portion. However, the identical properties of this substance, its similar behavior on fusion, the presence of benzoic acid in the filtrate after treating the fused mass with water, leave no doubt as to its being the same substance as that obtained by Remsen and Saunders from the solid chloride of orthosulphobenzoic acid, while the method of formation and the analysis prove that it has the structure



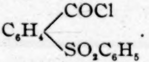
$$C_6H_4<\begin{matrix}COC_6H_5\\SO_2C_6H_5\end{matrix}.$$

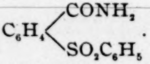
Conclusion.

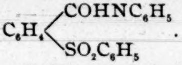
The results obtained in this investigation may be summarized thus :

1. By subjecting orthotoluenesulphone chloride to the Friedel-Crafts reaction, it readily passes into orthotolylphenylsulphone.

2. Employing potassium permanganate, this can be oxidized to orthophenylsulphonebenzoic acid, which forms well characterized salts.

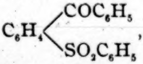
3. By means of phosphorus pentachloride the acid can be converted into the chloride,  $C_6H_4<\begin{matrix}COCl\\SO_2C_6H_5\end{matrix}.$

4. When treated with concentrated ammonia for twenty-four hours at ordinary temperature, the chloride yields an amide of the structure  $C_6H_4<\begin{matrix}CONH_2\\SO_2C_6H_5\end{matrix}.$

5. If to an emulsion of aniline and water orthophenylsulphonebenzoyl chloride is added, there is formed the anilide,  $C_6H_4<\begin{matrix}COHNC_6H_5\\SO_2C_6H_5\end{matrix}.$

6. By treating the chloride with benzene and aluminium chloride, another phenyl group can be introduced, though not

so readily as in the case of orthotoluenesulphone chloride. The new substance thus formed is orthobenzoyldiphenylsulphone, and is the same as that obtained by Remsen and Saunders by treating the chlorides of orthosulphobenzoic acid with benzene and aluminium chloride. Its structure is



$$C_6H_4\begin{cases} COC_6H_5 \\ SO_2C_6H_5 \end{cases}$$

, and in properties it differs markedly from the isomeric para-compound.

Contributions from the Chemical Laboratory of the Massachusetts Institute of Technology.

XXVIII.—ON THE IMPORTANCE OF FORMIC ALDEHYDE AS A PRODUCT OF THE PARTIAL COMBUSTION OF ORGANIC COMPOUNDS.

BY S. P. MULLIKEN, WITH J. W. BROWN AND P. R. FRENCH.

It has been shown elsewhere in this JOURNAL[1] by Mulliken and Scudder that formic aldehyde is apparently one of the most common products of the partial combustion of organic compounds by hot copper oxide, and that its appearance in minute traces as a result of such combustions ought never to be accepted as sufficient proof that the substance burned contains a methoxyl group. These conclusions were based entirely on qualitative experiments made incidentally in connection with a study of certain color tests for methyl alcohol. The present investigation is quantitative in character. Its object is to furnish direct proof that the quantities of formic aldehyde which may be obtained from the oxidation of various typical and purified non-methoxylated compounds are, in general, greater than could arise from accidental impurities in the substances used.

Before proceeding to a description of these experiments, allusion should be made to the few scattering earlier investigations which have a more or less direct bearing on the matter under consideration. Legler[2] claims to have found formic

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Vol. **24**, p. 446. Attention is here called to two slight corrections that should be made in the text of the article quoted. On page 451, line 21, insert the words "*containing strong sulphuric acid*," between "second tube" and "held,"; and on p. 452, line 18, read "*tertiary*," between "secondary" and "and butyl."

[2] Ann. Chem. (Liebig), **217**, 382; Ber. d. chem. Ges., **18**, 3343.

aldehyde in small quantities among the products of the phosphorescent combustion of ethyl ether in presence of metallic platinum. Pratesi[1] obtained it from a decomposition of the vapors of boiling ethyl nitrate induced by a strip of incandescent platinum. Its formation was detected by Schützenberger,[2] when ethylene was heated with oxygen to 400° ; and by Wolkow and by Menschutkin,[3] when a mixture of trimethylene and air was passed through a red-hot tube. Its occurrence to the extent of 0.5 per cent in wood smoke, which has lately been noted by Pasqualis,[4] may also be mentioned, although its appearance in this case is no doubt due merely to a secondary oxidation of the methyl alcohol, which is always formed when wood is subjected to destructive distillation.

In our experiments the oxidations were all made by means of the well-known, simple and efficient apparatus devised by Loew[5] for the preparation of formic aldehyde from methyl alcohol. Loew early used this apparatus for the partial oxidation of several non-methoxylated substances. Ethyl ether, ethyl acetate, and ethylamine, all gave him acetaldehyde, while toluene yielded some benzaldehyde ; but no substance other than methyl alcohol is mentioned as having given formic aldehyde, means for detecting small quantities of formic aldehyde in the presence of much acetic aldehyde being at that time unknown.

In Loew's method a stream of dry air, more or less fully saturated with a combustible vapor, is aspirated through a long tube of infusible glass containing a short coil of oxidized copper gauze, the latter being first brought nearly to redness by the temporary application of a gas flame. The copper oxide of the roll serving as an oxygen carrier, the roll continues to glow brightly, after the gas flame is withdrawn, as long as the combustible mixture is supplied. The liquefiable products of the reaction are condensed by passage through a series of well-cooled bottles containing water, which are interposed between the combustion tube and the suction-pump.

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[1] Gazz. chim. ital., **14**, 221.

[2] Bull. Soc. Chim., **31**, 482.

[3] Ber. d. chem. Ges., **31**, 3067.

[4] Centrbl., 1897, II., 1012.

[5] J. prakt. Chem., **33**, 324 ; cf. also Tollens in Ber. d. chem. Ges., **19**, 2135.

In our work the suction was supplied by a single Richards' water aspirator run at nearly its full capacity. The combustion tube was 2 feet long and supported near its lower end by a clamp protected by asbestos. The copper roll, 2 inches in length, was made of fine-meshed gauze rolled loosely to fill the whole bore of the tube. The space within the tube above the coil was filled with fibrous asbestos, as a precaution against possible explosions, though none ever occurred.

The aspirated air, after being first dried by sulphuric acid, was passed rapidly through the liquid with whose vapors it was to be charged. The liquid was placed in a round-bottomed flask supported at such a height that a water-bath might be brought under it to raise the temperature, if desired. An exit-tube passing through the stopper of this flask conveyed the mixture of air and vapor into the combustion tube. The latter was drawn out and bent at its lower end so as to just dip beneath the surface of 50 cc. of distilled water in the first of a series of four condensing bottles, each of which also contained water through which the gaseous combustion products were made to pass. Whenever a new vapor was to be burned, some preliminary experimenting was required to find the best temperature at which to maintain the evaporating liquid, and the proper rate at which to draw air through it. After the best conditions had been once ascertained, however, the combustion usually proceeded smoothly and with very little separation of carbon, the copper roll often maintaining its dull-red glow for several hours without requiring any special attention from the experimenter. A few moments' application of a Bunsen burner flame was frequently quite sufficient to start the reaction, though there were cases in which the heating had to be continued for more than fifteen minutes. The ratio between air and vapor in the different experiments could not readily be kept constant, and bore no known relation to the theoretical quantities corresponding to any particular chemical equations. The composition of the mixtures and the rate of aspiration were simply such as experience showed were favorable to uninterrupted combustion. In experiments with the same substance the largest yields of aldehyde were often obtained when only half the roll was glowing.

Considerable time was spent in the search for a reliable analytical method for the determination of small quantities of formic aldehyde in presence of much acetic aldehyde. In the course of this search Mr. Brown studied nearly all the methods that have been proposed for the analysis of formic aldehyde solutions, and came to the conclusion that acetic aldehyde must always first be removed. The method of separation which was adopted was based on the fact, referred to in the article by Mulliken and Scudder, that acetic aldehyde may be completely boiled out from dilute aqueous solutions in such a way that practically all of the formic aldehyde will be held back by the water. To accomplish this result in the present instance, the liquid contents of all the condenser bottles were united, diluted to 500 cc. with water, and placed in a round-bottomed liter flask connected with a long upright return-flow condenser. The upper end of the condenser was joined, by means of a descending glass tube, with a glass worm packed in ice and salt. The worm delivered into a flask surrounded by a freezing-mixture. The dilute aldehyde solution was gently boiled for two hours to drive over the acetic aldehyde. During the boiling, warm water at 45° to 50° was kept circulating through the condenser, the temperature being carefully controlled with the aid of a thermometer hung within the glass condenser-jacket. It was found, by direct experiments, that the quantity of formic aldehyde vapor which passed over and was absorbed by water placed in the cooled receiver upon boiling a 1 per cent aqueous solution for two hours, as above described, was too small to be accurately determined, though its presence in the receiver could be shown qualitatively by the delicate gallic acid test. The removal of acetic aldehyde by the process was so complete that in the experiment on the oxidation of ethyl alcohol, in which 43 grams of acetic aldehyde were produced, no trace of acetic aldehyde could be detected in the flask at the close of the two hours' boiling. A strong, unmistakable formalin odor, was, however, noticeable in each of the warm boiled solutions in which formic aldehyde was determined. These solutions also all gave very pronounced qualitative reactions for formic aldehyde, by the gallic acid, resorcin, and hexamethylenetetramine tetrabromide tests.

The determinations of formic aldehyde which follow were made by the colorimetric method of Trillat in essentially the form described by Wolff,[1] though with certain added precautions.

The determinations of acetic aldehyde were obtained by the colorimetric method of Thresh,[2] which was so far modified and improved as to give results which are trustworthy to within 2 per cent of their total value. Acetic aldehyde was tested for in all oxidation-products by adding solid sodic hydrate to a few centimeters of the mixed and diluted aqueous solutions until the liquid became almost syrupy, and then boiling for a minute or two. The least trace of acetic aldehyde then gave the characteristic aldehyde resin odor, and a deep-yellow solution.

The compounds chosen for oxidation were Kahlbaum's best preparations, and were carefully rectified before use by distillation through a tall Le Bel-Henninger tower. Only the middle portion of a large fraction of correct and constant boiling-point was used, unless it is otherwise stated in the record of the experiment. In the following brief statement of results the compounds studied follow one another in an order which corresponds to the quantity of formic aldehyde produced by their respective oxidations, the substance giving the largest yield closing the list. The experiments on acetone and ethyl alcohol were made by Mr. Brown, the remainder by Mr. French.

SUMMARY OF EXPERIMENTAL RESULTS.

Acetone.—(Prepared from the pure bisulphite compound.) 271 grams gave 0.6055 gram formic aldehyde, but no acetic aldehyde. Duration of oxidation, two and a half hours. Temperature of bath, 25° to 30°.—*Yield of formic aldehyde, 0.22 per cent.*

Ethyl Alcohol.—(Prepared from the purest absolute alcohol.) 187 grams gave 0.832 gram formic aldehyde and 42.9 grams acetic aldehyde. Duration of oxidation, three hours. Temperature of bath, 35° to 40°.—*Yield of formic aldehyde, 0.44 per cent.*

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[1] Ztschr. d. Nahr. u. Genuss., 1890, 89.

[2] Pharm. Jour. (3), 9, 408.

Pentane.—(Boiling-point 35° to 37°.) 119 grams gave 1.05 grams formic aldehyde, but no acetic aldehyde. No bath was employed.—*Yield of formic aldehyae, 0.88 per cent.*

Acetic Acid.—("99 to 100 per cent 'Kahlbaum's acid' free from homologues".) 232 grams with the bath at 60° to 65° gave 1.95 grams formic aldehyde, but no acetic aldehyde. The oxidation was very easily controlled and the copper roll no more disintegrated than in other experiments. Most of the unoxidized acid in the distillate was neutralized with calcium carbonate before determining the aldehyde.—*Yield of formic aldehyde, 0.84 per cent.*

Ethyl Oxide.—(Absolute ether distilled from sodium, boiling between 35° and 36°.) 258 grams gave 4.78 grams formic aldehyde and 12.24 grams acetaldehyde.—*Yield of formic aldehyde, 1.86 per cent.*

Amylene.—(Mainly trimethylethylene. Boiling-point 37° to 40°.) 100 grams gave 2.01 grams formic aldehyde, but no acetic aldehyde. No bath was used.—*Yield of formic aldehyde, 2.01 per cent.*

Normal Propyl Alcohol.—(Boiling-point 96° to 99°.) 56 grams with the bath at 45° to 50° gave 1.53 grams formic aldehyde, but no acetaldehyde.—*Yield of formic aldehyde, 2.72 per cent.*

Trimethylcarbinol.—(Boiling-point 82° to 85°.) 39 grams gave 2.01 grams formic aldehyde, but no acetaldehyde. Temperature of bath, 35° to 40°. The quantity of carbon dioxide formed in the experiment was unusually large.—*Yield of formic aldehyde, 5.17 per cent.*

An oxidation of 150 grams of benzene, free from thiophene, with the bath at 45° to 50°, did not give formic aldehyde in determinable quantity. The oxidation of an equal weight of toluene gave very appreciable quantities of formic aldehyde, but quantitative determinations were not attempted, as it was found that benzoic aldehyde, which was also present, would prevent the successful employment of the Trillat method.

In comparing the yields of formic aldehyde obtained in these experiments, it must be remembered that the values recorded hold true for a single set of conditions only, and that these cannot always have been the most favorable ones possible. The important fact demonstrated is the marked tendency to the production of measurable quantities of formic aldehyde in the partial combustion of numerous carbon compounds belonging to very dissimilar types. So far as yet appears, this reaction is even of more frequent occurrence in such oxidations by air and copper oxide as have been described, than is the more familiar formation of oxalic acid in oxidations by nitric acid. Whether formic aldehyde, in small quantities, is also a frequent product of oxidations in the wet way, we have not attempted to determine. That it may be formed in many reactions of this class is, however, not in the least improbable.

BOSTON, November 26, 1900.

XXIX.—ON THE NON-EXISTENCE OF TRIVALENT CARBON.

BY JAMES F. NORRIS.

In a paper which has recently appeared Gomberg[1] has reported the results of the study of the action of zinc on triphenylchlormethane. It was found that when a solution of the halogen compound in benzene was treated with zinc, a reaction took place slowly at ordinary temperatures and, if air was excluded, at the end of five or six days the chlorine was converted quantitatively into zinc chloride. There remained in solution a highly unsaturated substance which united with iodine at 0°, and was converted into an insoluble oxygen compound when brought into contact with the air. These reactions showed that the compound was not hexaphenylethane, the substance which would be expected as the result of the action of zinc on triphenylchlormethane. The author concluded that the properties of the unsaturated body could only be explained by assuming that it was a free radical. The reaction was expressed by the following equation:

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[1] J. Am. Chem. Soc., **22**, 757.

$$2(C_6H_5)_3CCl + Zn = 2(C_6H_5)_3C\text{—} + ZnCl_2.$$

Analyses and molecular weight determinations of the compound formed by the action of oxygen on the radical gave results which agreed with the formula

$$(C_6H_5)_3C\text{—}O\text{—}O\text{—}C(C_6H_5)_3.$$

As the result of the action of iodine on the radical, triphenyliodomethane was obtained.

In an attempt to prepare tetraphenylmethane in this laboratory by the action of sodium on a mixture of triphenylchlormethane and brombenzene, a preliminary account of which has already appeared,[1] it was found that an oxygen compound was one of the products of the reaction. In seeking the cause of the formation of an oxygen compound from substances containing no oxygen, we were led to study the action of sodium on triphenylchlormethane alone. As the explanation of the reaction which appeared probable to us was quite different from that proposed by Gomberg, and as it did not involve the assumption of a trivalent carbon atom, it seemed important to test the theory by studying the reaction described by Gomberg. As a result, facts have been discovered which furnish an adequate explanation of the reaction without the necessity of introducing any new principles.

It seemed probable that when zinc reacted with triphenylchlormethane, the metal caused the elimination of hydrogen chloride and not of chlorine alone. This common action of zinc on halogen compounds is shown in the case of the compounds $C_6H_5CH_2Cl$ and $(C_6H_5)_2CHCl$. In the case of triphenylchlormethane the elimination of hydrogen chloride would involve the removal of a hydrogen atom from a benzene ring and not from the methane carbon, as is the case with the two compounds cited. Such a loss of hydrogen chloride has already been observed. Hemilian[2] showed that when triphenylchlormethane was heated to 200°, hydrogen chloride was split off, and among the products formed was a hydrocarbon to which he assigned the formula $(C_6H_5)_2C : C_6H_4$. E. and O. Fischer[3] showed later that the substance had the formula

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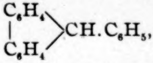
[1] This JOURNAL, **25**, 54.

[2] Ber. d. chem. Ges., **7**, 1208.

[3] Ann. Chem. (Liebig), **194**, 256.



by preparing it by the condensation of fluorene alcohol and benzene. Hanriot[1] has assigned the formula $(C_6H_5)_2C : C_6H_4$ to a hydrocarbon formed by the action of potassium on triphenylmethane at 300°. This hydrocarbon is probably identical with the one prepared by Hemilian, as it resembles it closely and does not show the reactions of an unsaturated compound. It is possible that in both cases a substance having the structure suggested by Hemilian was first formed, and that this at the high temperature suffered a molecular rearrangement into the fluorene derivative.

The properties and reactions of triphenylchlormethane are being studied in this laboratory by Mr. Erik Green, who has shown that the compound readily loses hydrogen chloride. When it is treated with concentrated sulphuric acid it goes into solution without rise in temperature, and hydrogen chloride is evolved in large quantities.

When zinc acts upon triphenylchlormethane dissolved in benzene there is no evolution of hydrogen and zinc chloride is formed. This fact does not speak against the theory that the metal removes hydrogen chloride, for the nascent hydrogen formed by the action of the acid on the zinc, as it is produced very slowly during five days, might add itself completely to either a part of the unsaturated compound produced by the reaction or to the benzene used as a solvent. An experiment described below seems to indicate that the latter view is probably correct.

As ethyl acetate is known to have a marked effect on the removal of halogens from their compounds by means of metals, the action of zinc on triphenylchlormethane dissolved in this solvent was studied. It was found that the reaction started in a few seconds and was complete in two to three minutes. In this case, if air was excluded, a solution was obtained in which a white precipitate was formed when it was brought into contact with the air. This precipitate was shown to be identical with the peroxide obtained when the solvent was benzene. When crystallized from carbon disulphide the characteristic hexagonal plates, which have a high index of refraction, were obtained. The reaction was evidently the same as that in benzene solution with the exception that in ethyl acetate the reaction was complete in a few minutes, whereas in benzene, five to six days were required. Further, when ethyl acetate was the solvent, hydrogen was evolved and hydrochloric acid was formed in the solution. An experiment was carried out in the following manner: To about 1 gram of pure, colorless triphenylchlormethane, dissolved in 5 cc. of ethyl acetate, which had been previously shaken with sodium carbonate to remove free acetic acid, was added about 1 gram of powdered zinc. In a short time the solution assumed a pale-yellow color and a gas was given off, which was shown to be hydrogen. As the reaction proceeded the yellow color of the solution increased in depth until it approximated that of a dilute solution of potassium chromate. When the reaction was complete the solution was shaken in contact with the air. A white precipitate was formed and the solution lost its yellow color. The ethyl acetate was found to be acid and to contain zinc chloride. It was shown that zinc has no action upon ethyl acetate under the conditions used in this experiment.

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[1] Bull. Soc. Chim. [3], 1, 775.

In this experiment the white precipitate, which was shown to be identical with that formed from a benzene solution of the unsaturated compound, was produced by the action of the air on a substance which was formed as the result of the elimination of hydrogen chloride from triphenylchlormethane. It follows, therefore, that in a benzene solution the same reaction takes place. The following equation appears to represent the facts:

$$2(C_6H_5)_3C.Cl + Zn = 2(C_6H_5)_2C : C_6H_4 + ZnCl_2 + H_2.$$

When ethyl acetate is the solvent less than one-fourth of the theoretical amount of hydrogen is set free, the remainder stays in solution as hydrochloric acid.

When benzene is the solvent the hydrogen is probably added to the benzene, for no triphenylmethane was found in solution after the peroxide was filtered off. The following experiment appears to furnish evidence in favor of this view.

Sodium was added to ether which contained a small quantity of water, and the amount of hydrogen evolved was noted. Some benzene was now added. The evolution of gas was reduced to the extent of almost one-half. The experiment was repeated, using naphthalene instead of benzene. The same result was observed. It has been shown by Bamberger that when naphthalene is added to alcohol containing sodium it is reduced. In the experiment just described it is probable that the naphthalene and the benzene united with a part of the evolved hydrogen.[1]

Gomberg has shown that the structure of the oxide formed by the action of oxygen on the unsaturated compound is best expressed by the formula

$$(C_6H_5)_3C—O—O—C(C_6H_5)_3.$$

A body with this structure could not be produced by the action of oxygen alone on diphenylphenylenemethane,

$$(C_6H_5)_2C : C_6H_4.$$

It might result, however, by the combined action of water and oxygen, or by the action of hydrogen peroxide. An experiment made to test this point showed that the unsaturated hydrocarbon does not unite with dry oxygen. A stream of dry air was drawn through a benzene solution of the compound for twenty minutes and no precipitate was formed. When the solution was exposed to the air the oxide began to separate in a few seconds. When an ethereal solution of hydrogen peroxide and a solution of the unsaturated hydrocarbon in ethyl acetate were mixed, care being taken to avoid the presence of air, a precipitate was slowly formed. The formulas given for the hydrocarbon and the oxide are, therefore, an expression of these facts.

By the action of iodine on the unsaturated compound, Gomberg obtained triphenyliodomethane. The formation of this compound from a substance of the structure $(C_6H_5)_2C : C_6H_4$ could be brought about only by the addition of hydrogen iodide. Even at 0°, in addition to direct addition, substitution with the consequent formation of hydrogen iodide would be expected when such a highly unsaturated compound is treated with iodine. Iodine readily substitutes in compounds which unite with hydrogen iodide. Aniline forms an iodo derivative and methylamine is converted in part into methylamine hydroiodide when it is treated with iodine at 0°.

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[1] As the benzene used contained thiophene the hydrogen may have been absorbed by it.

All of the reactions of the substance formed by the action of zinc on triphenylchlormethane are easily explained if the compound so formed is diphenylphenylenemethane,

$$(C_6H_5)_2C : C_6H_4.$$

It is of interest to mention the fact that tetrahydronaphthalene resembles diphenylphenylenemethane in some of its properties. It is reduced with difficulty, it absorbs oxygen from the air, and unites with the halogens at low temperatures, halogen hydrides being formed at the same time.

If the structure here proposed is correct, the compound is of unusual interest, as it contains a carbon atom which is linked to two carbon atoms in a single benzene ring. This structure is put forward tentatively. It is an expression of the reactions of the compounds as far as they have been studied, but further work is necessary before it can be accepted. The double-linking between the methane carbon and the benzene ring may resemble that between the carbon and nitrogen atoms in the triphenylmethane dyes. The fact that the compound is colored, indicates that it may have such a quinoid structure. This view will be tested by studying the action of metals on trinitrotriphenylchlormethane, in which the three places in the benzene rings para to the methane carbon, are occupied by nitro groups. The compound may have double the molecular weight of the formula given, in which case it would have a structure somewhat like the accepted quinone structure.

As ethyl acetate has been found to have such a marked influence on the action of zinc on triphenylchlormethane, the action of metals on other halogen compounds dissolved in ethyl acetate will be investigated in this laboratory.

BOSTON, MASS., December 6, 1900.

THE CONSTITUTION OF BENZENE.

BY GEORGE M. RICHARDSON.

The work of Baeyer[1] upon the constitution of benzene has shown that Ladenburg's prism formula for benzene is extremely improbable; but this work did not enable Baeyer to decide definitely for or against either the Kekulé or Claus formula.

The Kekulé formula, showing as it does the occurrence of the ethylene condition three times in the benzene nucleus, is in many respects unsatisfactory, for benzene does not show the properties that we are accustomed to ascribe to the ethylene condition, either in its conduct towards the halogen acids or its behavior towards oxidizing agents.

Claus,[2] in order to avoid Ladenburg's objection to his formula that the ortho and para positions are identical, found it necessary to assume that the para bond is essentially unlike the ortho bond. In so doing, Claus necessarily introduced geometrical conceptions in regard to the molecule, ideas which at that time were not favorably received.[3]

Now that geometrical conceptions are continually being taken into account in the consideration of the structure of carbon compounds, Claus' assumptions do not seem so forced as they once did.

Baeyer has shown then when two hydrogen atoms are added to terephthalic acid they take the para position with regard to one another, as is indicated by the Claus formula.

When two hydrogen atoms are added to dihydroterephthalic acid, they do not go para to one another, but go to the ortho position, showing that in dihydroterephthalic acid there are no para bonds, but instead double linking. This caused Claus[4] to further modify his views by assuming that when the first para bond is broken the two remaining para bonds rearrange themselves to double linking.

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[1] Ann. Chem. (Liebig) **245**, 103; **251**, 257; **256**, 1; **258**, 1; **258**, 145: **266**, 169; **269**, 145; **276**, 255. This work of Baeyer's is well summarized in his address on the occasion of the Kekulé celebration, Ber. d. chem. Ges., **23**, 1277 (1890).

[2] Ber. d. chem. Ges., **15**, 1405.

[3] See Richard Meyer: Ber. d. chem. Ges., **15**, 1826.

[4] J. prakt. Chem., **145**, 455 (1888).

In ethylene compounds, it is not an uncommon experience to find that the ethylene condition has shifted its position in the course of a chemical reaction. Certain work with muconic acid convinced Baeyer[1] that, even were the Kekulé formula true, in the course of the reduction the position of the double linking would be so readjusted that the first pair of hydrogen atoms added to terephthalic acid would take the para position instead of the ortho position.

The impossibility of getting positive evidence in favor of either Kekulé's formula or Claus' formula, and the lack of entire satisfaction with either of these formulas, led Baeyer[2] to advance the "Centric formula" shortly before suggested by Armstrong.[3] This is a modified Claus formula in which the fourth valence of each carbon atom is supposed to be directed toward the center of the system, but instead of being in combination with the corresponding valence of the para carbon atoms, it is in some unknown manner held in a state of stable equilibrium by the other five similar valences without being necessarily in combination with any one of them. When a pair of these bonds is removed, as by the addition of two hydrogen atoms, the equilibrium is destroyed and the remaining bonds readjust themselves in some new manner.

By its very nature, this suggestion is incapable of experimental proof. It has, however, the distinct advantage of being a peculiar kind of formula for a peculiar kind of condition, and of being vague just where actual knowledge is vague, and therefore under the present conditions of our knowledge, is perhaps the most satisfactory formula for benzene.

It has seemed to the writer, however, that one feature of the Claus formula, which is lost by merging it into the centric formula, is worth preserving, since it is in accord with a large number of facts. The feature referred to is the expression of a relationship between ortho and para compounds, since these compounds stand together in many chemical reactions as distinguished from meta compounds. It is the purpose of this paper to call attention to this class of phenomena in greater detail than has before been done, and thereby to raise the question, whether, all things considered, the Claus formula does not better represent the structure of benzene than any other formula yet advanced.

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[1] Ann. Chem. (Liebig) **256**, 1. See also Baeyer's address at the Kekulé celebration, Ber. d. chem. Ges., **23**, 1277.

[2] Ann. Chem. (Liebig), **245**, 127.

[3] J. Chem. Soc., **51**, 263 (1887).

The phenomena to be considered will be taken up under the four heads: *I. The Phenomena of Substitution; II. The Effect of Position of the Substituting Groups upon the Properties of a Compound; III. The Phenomena of Reduction;* and *IV. The Phenomena of Oxidation.*

I. *The Phenomena of Substitution in the Benzene Nucleus.*[1]

When reagents, which are capable of replacing the hydrogen of the benzene nucleus, act upon monosubstitution products of benzene to form disubstitution products, the position assumed by the entering element or group is governed by the character of the group already present in the monosubstitution product.

If the group already present is a halogen element, or has a basic character, such as Cl, Br, I, CH_3, CH_2Cl, $CHCl_2$, CCl_3, OH, NH_2, NHAc, NH_2HCl, CH_2COOH, CHCHCOOH, the new element or group entering takes the ortho- or para-position. Usually both ortho and para compounds are formed simultaneously, sometimes one in excess and sometimes the other, the proportions between the two being frequently more or less controlled by the conditions of the experiment.

On the other hand, if the group present in the monosubstitution product has an acid character (the halogen elements being excepted), such as: NO_2, CN, COOH, CHO, $COCH_3$, $COCH_2Br$, COC_6H_5, SO_2OH, $SO_2C_6H_5$, the second entering group takes the meta-position.

From this it would seem that the ortho and para positions have something in common which distinguishes them from the meta position. This relation is expressed better by the Claus formula than by any of the other benzene formulas now in use.

From this formula (Fig. I.), it will be seen that carbon atom 1 is in direct combination with carbon atoms 2, 6, and

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[1] Armstrong (J. Chem. Soc., **51**, 258, 579, and 583) has considered the laws of substitution and their bearing on the structure of benzene, but the conclusions reached differ materially from those developed here.

4, while with carbon atoms 3 and 5, it is not in direct combination. Ladenburg's prism formula (Fig. II.), or the modified prism or star formula (Fig. III.), indicating as they do, a direct combination between carbon atoms 1 and 3, 1 and 5, 1 and 4, and hence, a similarity between meta and para compounds as distinguished from the ortho compounds, is not so well in accord with the facts.

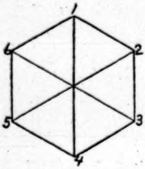


Fig. I.

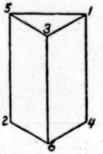


Fig. II.

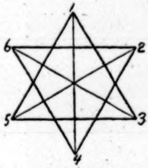


Fig. III.

Now if position 1 in the Claus formula is occupied by a basic group, the action of acid reagents upon that carbon atom will be increased, but in this case there is no more hydrogen attached to carbon atom 1 to be replaced, so the acid reagents act upon those carbon atoms most intimately related to carbon atom 1, that is, upon those in direct combination with it, and replaces the hydrogen atoms attached to carbon atoms 2, 6, or 4, to form ortho and para compounds.

If, however, position 1 is occupied by an acid group (chlorine, bromine, and iodine being excepted, since these cause the formation of ortho and para compounds) it would render carbon atom 1 less susceptible to the action of acid reagents, and this influence would extend to the carbon atoms immediately connected with carbon atom 1; that is, to carbon atoms 2, 6, and 4. Carbon atoms 3 and 5 would therefore of the whole molecule be the atoms most likely to be attacked by the acid reagent; that is, meta compounds would be formed.

If these suggestions as to the cause of the phenomena observed are correct, it seems probable that if the second entering group were of a basic character, or of such a character as to be attracted by acid groups already present in the monosubstitution product, acid groups would cause the formation of ortho and para compounds instead of meta compounds, and basic groups would cause the formation of meta compounds instead of ortho and para compounds. This point cannot at present be experimentally tested, as we do not know any basic group that can be substituted for the hydrogen of benzene by direct action of a substituting agent. The formation of resorcin by fusing with caustic potash at high temperatures both the ortho- and parabrombenzenesulphonic acid, as well as the corresponding meta compound, and the preponderance of metaxylene in coal-tar are phenomena that may be due to this cause.

In a general way we think of an acid group and a basic group as having an attraction for one another, and think of two groups of the same kind, two acid groups or two basic groups as having little or no attraction for one another, or even as having a repulsion for one another. Doubtless in the main such assumptions are correct, but that such is uniformly the case cannot safely be assumed.

Our knowledge of the preference which organic groups have for each other, or for other elements is very imperfect.

This point has been considered in the discussion on the "most favorable configuration" of organic molecules containing two singly linked asymmetric carbon atoms, and the lack of exact information is well illustrated by the lack of unanimity in the opinion of the most prominent workers in this field. Wislicenus assumes that methyl groups do not attract one another, but that they repel one another. Bischoff assumes that the repulsion is very weak between the methyl groups, while Baeyer assumes that methyl groups attract one another. Bischoff has assumed a repulsion between methyl and carboxyl, while other writers have assumed that these groups attract each other.

It is nevertheless rather surprising to find the halogen elements acting with the basic groups, and according to the views here expressed, attracting other halogen elements and acid groups, causing the formation of ortho and para compounds instead of meta compounds. But that they are attractive to other halogen elements, and to acid groups when combined with carbon, seems to be true, judging from their behavior in the paraffin series.

When hydrochloric acid is added to an unsaturated ethylene hydrocarbon, the chlorine goes to the carbon atom which is combined with the least hydrogen; *e.g.*, $CH_2CH\ CH_3$ gives $CH_3CHClCH_3$, and not $CH_2ClCH_2CH_3$.

When the two unsaturated carbon atoms hold the same amount of hydrogen, the chlorine goes to that carbon atom holding the simplest radical; *e.g.*, $CH_3CHCHCH_2CH_3$ gives $CH_3CHClCH_2CH_2CH_3$, and not $CH_3CH_2CHClCH_2CH_3$, in this case illustrating the greater affinity of chlorine for methyl than for ethyl. A corresponding phenomenon in the benzene series is seen when the halogens act upon cymene or para-ethyl toluene; the halogen element always assumes a position ortho to the methyl, and meta to the more complex radical.

In the ethylene series if one of the unsaturated carbon atoms is attached to chlorine, the second chlorine atom will go to the same carbon atom; *e.g.*, CH_2CHCl gives with hydrochloric acid, CH_3CHCl_2, and not CH_2ClCH_2Cl, thus illustrating the power of chlorine to attract chlorine.

Other acid groups appear to repel the chlorine; *e.g.*, $CH_2CHCOOH$ gives CH_2ClCH_2COOH and not CH_3CHCl $COOH$; this fact is frequently utilized in the preparation of β-chlor acids, and is parallel to the formation of meta-compounds in the benzene series under similar conditions.

In chlorinating saturated hydrocarbons, the first chlorine atom will go to the carbon atom in combination with the least hydrogen; if, however, one chlorine atom is already in the compound, the second chlorine atom wherever possible will go to the same carbon atom, or to the carbon atom immediately adjoining.

As is well known, it is more difficult to chlorinate acetic acid than it is to chlorinate marsh gas, the difference being due presumably to the lack of affinity between the chlorine and the carboxyl group. Acetyl chloride is, however, easier to chlorinate than acetic acid, illustrating again the favorable action of chlorine already present in a compound upon the chlorination process.

The direct chlorination of propionic acid gives α-chlor-propionic acid. Here the tendency of the chlorine atom to go to the carbon atom which is in combination with the least hydrogen (due perhaps to the attractive power of the methyl group which is in combination with that carbon atom), is greater than the retarding influence of the carboxyl group. With normal butyric acid, $CH_3CH_2CH_2COOH$, direct chlorination gives β-chlorbutyric acid, $CH_3CHClCH_2COOH$, both the carboxyl and the methyl groups tend to cause the chlorine to take this position.

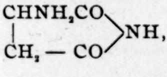
If, however, butyryl chloride, $CH_3CH_2CH_2COCl$, is chlorinated, α-chlorbutyryl chloride, $CH_3CH_2CHClCOCl$, is obtained, again illustrating the power of chlorine to attract chlorine.

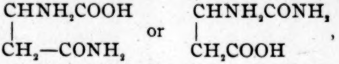
With chlorine and hydrochloric acid, the tendencies here mentioned are so strong, that isomeric modifications are seldom formed. With bromine and hydrobromic acid, with iodine and hydriodic acid, the same tendencies are observed, but in a less marked degree; so that as a rule isomeric modifications are formed; *e. g.*, CH_3CHCH_2 gives with hydrobromic acid both $CH_3CHBrCH_3$ and $CH_3CH_2CH_2Br$, but the former is the chief product of the reaction. Parallel to this we find in the benzene series that the chlorination of benzoic acid gives only metachlorbenzoic acid, while the bromination of benzoic acid gives chiefly metabrombenzoic acid, but also gives some orthobrombenzoic acid.

The fact that the acid chlorides are easier to chlorinate than the free acids, and that they tend to form α-chlorderivatives, suggests the possibility that in the chlorination of benzoyl chloride, some ortho chlorbenzoyl chloride might be formed, and in the bromination of benzoyl bromide the yield of the ortho compound might be increased. Too little is known with regard to the substituting action of other agents than the halogens in the paraffin series to give any general rules.

The addition of water to the imides of the substituted dibasic acids might give some evidence on the point of attraction and repulsion between various organic radicals.

The imide of aspartic acid, for example,





takes up water to form $\begin{array}{l} CHNH_2COOH \\ | \\ CH_2-CONH_2 \end{array}$ or $\begin{array}{l} CHNH_2CONH_2 \\ | \\ CH_2COOH \end{array}$, or both. In this particular case it is believed that the former compound is formed rather than the latter. An inspection of the formula with a consideration of the probable attractions and repulsions would indicate that the carboxyl group would go to the carbon holding the amido group, or that the two amido groups, other things being equal, would tend to be as far apart as possible.

Too few examples of this kind of action have yet been examined to permit of any conclusions being based upon them.

So far as our present experience goes, the facts appear to be in accordance with the following generalization:

If the group present in the benzene nucleus attracts the entering group, it will form ortho and para compounds. If, on the other hand, it repels the entering group, meta compounds will be formed. When the attraction or repulsion between the groups is not marked, all three classes of compounds may be formed simultaneously.

II. The Effect of the Position of the Substituting Groups upon the Properties of the Compound.

Halogen elements held in the benzene nucleus are not usually replaced by the amido group by the action of ammonia, or replaced by hydroxyl, by the action of potassium hydroxide.

If, however, the halogen element has a nitro group, ortho or para to it, it may then be replaced by the amido group by the action of ammonia, or by the hydroxyl group by the action of potassium hydroxide. If the nitro group is in the meta position with regard to the halogen element, it has much less influence upon the halogen element, for such a halogen element is not acted upon by ammonia or caustic potash. A nitro group attached to a carbon atom weakens the hold of other electronegative atoms upon that carbon atom. This kind of influence may even extend to the carbon atoms immediately connected with the carbon atom holding the nitro group.[1] Hence, in the Claus formula, if a nitro group is in the position, 2, 6, or 4, it would weaken the hold of the chlorine upon carbon atom 1. A nitro group attached to carbon atom 3 or 5 (that is in the meta position), since these carbon atoms are not in direct combination with carbon atom 1, would have much less action upon the chlorine attached to carbon atom 1.

The fact that one group exerts a stronger influence over another when in the ortho- or para-position with regard to it, than when in the meta-position with regard to it, may be farther illustrated.

The presence of a nitro group in a compound tends to increase its acid properties, or to decrease its basic properties, as for example, the nitrophenols are much stronger acids than phenol itself, and the nitroanilines are much weaker bases than aniline. Ortho- and para-nitrophenol are strong acids, much stronger than the metanitrophenol, which is only a slightly stronger acid than phenol.

From an examination of the possible formulas for the trinitrophenols, we should choose that of picric acid, $C_6H_2OHNO_2NO_2NO_2$ (1, 2, 4, 6,), as the one representing the strongest acid properties, and this appears to be in accordance with the facts.

Of the three nitranilines, ortho- and para-nitraniline are very weak bases, their salts being decomposed by water.

Meta-nitraniline is a much stronger base; it salts may be crystallized from water without decomposition.

Ortho-nitrobenzoic acid is the strongest of the three nitrobenzoic acids.

In so far as the data of this class are considered, it is practically impossible to decide between the ortho- and para-positions, as to which of these is the position of greatest influence, for in some cases it seems to be one, and in some cases the other. Also with the substitution products, sometimes it is the ortho compound that is formed in the greater quantity, and sometimes it is the para compound. If the Claus formula were to be accepted as correct, even then it would be very difficult to say which would have the greater influence. It must be assumed that the para bond of the Claus formula is weaker than the ortho bond, since it is always the para bond that is broken in the formation of addition products. It might well be that the same cause which weakens the para bond would also tend to weaken the influence of a group in the para position as compared with its influence in the ortho position. However, this may be, we now come to consider a class of phenomena, where, with very few exceptions, groups in the ortho position are seen to have a greater influence than when in the para position, and groups in the para position have a greater influence than when in the meta position.

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[1] That groups which are attached to a carbon atom may have an influence upon the affinity of carbon atoms immediately adjoining, is frequently assumed. As an example, we may take the assumption made with regard to chloral hydrate, the formula of which is written, $CCl_3CH(OH)_2$. Here the unusual power which enables one carbon atom to hold in combination two hydroxyl groups is attributed to the influence of the three chlorine atoms which are in combination with the neighboring carbon atom.

III. The Phenomena of Reduction.

If we were to draw any conclusions in regard to the processes of reduction from the conceptions advanced here, they would be as follows: The presence of a substituting group in a benzene compound which also contained a reducible group, as for example, nitrobenzene would increase the ease of reduction of the nitro-group if the substituting group were of a character to attract the reducing agent, and would increase the difficulty of reduction if the substituting group were of such a character as to repel the reducing agent. Moreover, the substituting group would presumably produce its maximum effect when ortho to the reducible group, a somewhat less but similar effect when para to the reducible group, and a much less effect, or perhaps no appreciable effect at all, when in the meta-position with regard to the reducible group.

In a general way we think of basic groups as being attractive to acid reducing agents, and non-attractive to alkaline reducing agents; and of acid groups as being attractive to alkaline reducing agents and non-attractive to acid reducing agents. That there may be exceptions to this classification is quite probable. We have already seen that the acid halogen elements, when combined with carbon appear to have an attraction for other halogen elements and for acid groups.

There is a large amount of data scattered through the chemical literature in regard to the reduction of benzene compounds, but so far as I can learn it has never been brought together and few generalizations have been made in regard to it. I shall present here some of the facts in regard to the reduction of nitro compounds with tin and hydrochloric acid; with stannous chloride and hydrochloric acid; with hydrogen sulphide in ammonia solution; and with ammonia itself in aqueous or alcoholic solution.[1]

It may be said at once that the results thus far brought together confirm in a most striking manner the generalizations made above.

Tin and hydrochloric acid[2] will reduce all of the nitro groups present in a compound, and in all situations.

No group acid or basic is capable of protecting a nitro group from reduction by these reagents. The same is true of stannous chloride and hydrochloric acid. When a compound contains two or more nitro groups the nitro groups may be reduced one at a time by using the proper amounts of tin or of stannous chloride (the latter is more satisfactory for partial reductions in actual practice). By noting the order in which the nitro groups are selected for reduction by the reducing agent, we can get evidence on the points in question. As to the order of selection tin and stannous chloride in hydrochloric acid behave precisely alike, as would be expected.

When di- and trinitrobenzene compounds are reduced by hydrogen sulphide in ammonia solution only one nitro group is reduced at first, a second nitro group may or may not be reduced by this reagent, depending upon the nature of the other groups present. The reduction of the second group is favored by the accumulation of negative groups in the compound, especially if in the ortho or para position with reference to the nitro group to be reduced. It is hindered or altogether prevented by basic groups ortho or para to the nitro group. The protective power of an amido group ortho to a nitro group is especially marked so far as this reducing agent is concerned.

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[1] Most of the facts here given have been collected for me by Mr. W. D. Harkins.

[2] Ber. d. chem. Ges., **11**, 35 and 40; **20**, 1567; **19**, 2161.

Ammonia in aqueous or alcoholic solution is frequently used to convert the nitro group into the amido group. It is probable that this is not a true reduction but rather an exchange of the nitro group for the amido group, according to the equation:

$$C_6H_4NO_2NO_2 + NH_3 = C_6H_4NO_2NH_2 + HNO_2 \text{ or}$$
$$C_6H_4NO_2NO_2 + 2NH_3 =$$
$$C_6H_4NO_2NH_2 + (NH_4NO_2) = 2H_2O + 2N.$$

It is known for example that, if the nitro group is ortho or para to chlorine, it is the chlorine and not the nitro group that is replaced by the amido group. Whether the reaction be a true reduction or merely an exchange of the nitro group for an amido group, the evidence furnished upon the points in question is the same.

(1) *Influence of Methyl Group upon the Reduction of the Nitro Group.*

Beilstein and Kuhlberg[1] have shown that dinitrotoluene, $C_6H_3CH_3NO_2NO_2$ (1, 2, 4), when reduced with ammonium sulphide, gives nitroparatoluidine, $C_6H_3CH_3NO_2NH_2$ (1, 2, 4).

Anschütz and Heusler[2] have shown that the same dinitrotoluene, $C_6H_3CH_3NO_2NO_2$ (1, 2, 4), when reduced with stannous chloride and hydrochloric acid, gives nitro orthotoluidine, $C_6H_3CH_3NH_2NO_2$ (1, 2, 4) without a trace of the isomer formed when ammonium sulphide is used as a reducing agent.

Cunerth[3] states that the dinitrotoluene, $C_6H_3CH_3NO_2NO_2$ (1, 2, 5), when reduced with ammonium sulphide, gives the nitrometatoluidine, $C_6H_3CH_3NO_2NH_2$ (1, 2, 5).

Tiemann[4] has shown that trinitrotoluene, $C_6H_2CH_3NO_2NO_2NO_2$ (1, 2, 4, 6), when reduced with ammonium sulphide, gives dinitroparatoluidine, $C_6H_2CH_3NO_2NH_2NO_2$ (1, 2, 4, 6), and the trinitro toluene, $C_6H_2CH_3NO_2NO_2NO_2$ (1, 3, 4, 6), gives with alcoholic ammonia dinitrometatoluidine, $C_6H_2CH_3NH_2NO_2NO_2$ (1, 3, 4, 6).

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[1] Ann. Chem. (Liebig), **155**, 14.

[2] Ber. d. chem. Ges. **19**, 2161.

[3] Ann. Chem. (Liebig), **172**, 223.

[4] Ber. d. chem. Ges., **3**, 218.

Grevingk[1] finds that dinitrometaxylene, $C_6H_2CH_3NO_2CH_3NO_2$ (1, 2, 3, 4), when reduced with ammonium sulphide, gives the nitroxylidine, $C_6H_2CH_3NO_2CH_3NH_2$ (1, 2, 3, 4).

Fittig[2] states that the dinitroparaxylene, $C_6H_2CH_3NO_2CH_3NO_2$ (1, 2, 4, 5,), when reduced with ammonium sulphide, gives the nitroxylidine, $C_6H_2CH_3NH_2CH_3NO_2$ (1, 2, 4, 5), and the dinitroparaxylidine, $C_6H_2CH_3NO_2CH_3NO_2$ (1, 2, 4, 6), when reduced with ammonium sulphide, gives the nitroxylidine, $C_6H_2CH_3NH_2CH_3NO_2$ (1, 2, 4, 6), but that the former of these, is reduced much more easily than the latter. In both these cases the nitro groups are ortho to one methyl group and para to the other, so that the methyl groups would not effect the comparative ease of reductions of the two compounds. It seems therefore, that the difference must be due to the different relations of the two nitro groups to each other in the two compounds, and we should infer that the nitro group must aid reduction with ammonium sulphide more when in the para position than when in the meta position.

In every case which has come under my notice the methyl group seems to have the effect predicted for it upon reducing agents.

(2). *Influence of Chlorine upon the Reduction of Nitro Groups.*

Beilstein[3] states that orthochlornitrobenzene is not reduced by ammonium sulphide, while the para- and metachlornitrobenzene are reduced.

Claus and Stiebel[4] found that the chlordinitrobenzene, $C_6H_3ClNO_2NO_2$ (1, 2, 4), when reduced with stannous chloride and hydrochloric acid, gave as the chief product the chlornitraniline, $C_6H_3ClNH_2NO_2$ (1, 2, 4); but at the same time a small amount of the isomeric chlornitraniline, $C_6H_3ClNO_2NH_2$ (1, 2, 4), was formed.

Laubenheimer[5] states that the chlordinitrobenzene, $C_6H_3ClNO_2NO_2$ (1, 3, 4), when heated with ammonia, gives the chlornitraniline, $C_6H_3ClNH_2NO_2$ (1, 3, 4). Here the fact that one nitro group is replaced by an amido group is doubtless due to the favorable action of the second nitro group ortho to the nitro group replaced, for the metachlornitrobenzene, $C_6H_4ClNO_2$ (1, 3), is not acted upon by ammonia. But the chlorine apparently exerts a sufficient retarding influence upon the action of the ammonia to cause the nitro group meta to the chlorine to be selected rather than the nitro group para to the chlorine.

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[1] Ber. d. chem. Ges., **17**, 2425.

[2] Ann. Chem. (Liebig), **147**, 18 and 22.

[3] Ber. d. chem. Ges., **11**, 2056.

[4] Ber. d. chem. Ges., **20**, 1379.

Ber. d. chem. Ges., **9**, 1826.

From all the data found in regard to the action of chlorine upon the reduction of the nitro group, it appears that chlorine ortho to a nitro group favors its reduction with acid reducing agents and retards its reduction with alkaline reducing agents. Hence chlorine acts here with the basic elements as it does in the phenomena of substitution.

(3) *Influence of Hydroxyl Groups upon the Reduction of Nitro Groups.*

Stuckenberg[1] has shown that dinitrophenol, $C_6H_3OHNO_2NO_2$ (1, 2, 4,), when reduced with ammonium sulphide, gives the nitroamidophenol, $C_6H_3OHNH_2NO_2$ (1, 2, 4).

Griess[2] states that the chlordinitrophenol, $C_6H_2OHNO_2NO_2Cl$ (1, 2, 4, 6), when reduced with ammonium sulphide gives the chlornitroamidophenol, $C_6H_2OHNH_2NO_2Cl$ (1, 2, 4, 6).

Picric acid[3] when reduced with ammonium sulphide, or with alkaline solutions of ferrous sulphate, or with an acetic acid solution of ferrous salts has one of the nitro groups, that is ortho to the hydroxyl group reduced. The second ortho nitro group may also be reduced by ammonium sulphide.[4]

Data concerning the partial reduction of the polynitrophenols with acid reducing agents, we have not been able to find with the exception of the partial reduction of picric acid with acetic acid solution of ferrous salts mentioned above.

Finding that hydroxyl acts with the basic groups in the formation of substitution products, according to the views here set forth, we should expect it to favor the action of acid reducing agents. From the data given above, it evidently favors the action of alkaline reducing agents. In hydroxyl, then, we have a group that appears to be attractive to both acid and alkaline reagents.

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[1] Ann. Chem. (Liebig), **205**, 72.

[2] *Ibid.*, **109**, 291.

[3] Girard: Compt. rend., **36**, 421; **42**, 59. See also Pugh: Ann. Chem. (Liebig), **96**, 83.

[4] Griess: Ann. Chem. (Liebig), **154**, 202.

(4) *Influence of the Sulphonic Acid Group upon the Reduction of the Nitro Group.*

The only case that we have been able to find that would bear on this point, is that of the partial reduction of the dinitrobenzenesulphonic acid, $C_6H_3SO_3HNO_2NO_2$ (1, 2, 4,), mentioned by Nietzki and Helbach,[1] and which gives the nitroamidobenzenesulphonic acid, $C_6H_3SO_2HNO_2NH_2$ (1, 2, 4), but unfortunately the authors do not mention the reducing agent used.

(5) *Influence of the Carboxyl Group upon the Reduction of the Nitro Group.*

Ortho- and paranitrobenzoic acids are much easier to reduce with ammonium sulphide than metanitrobenzoic acid.

Little other evidence on the effect of the carboxyl group has been found, as in those cases where data were found the nitro groups were symmetrically situated with regard to the carboxyl group and so gave no evidence upon the point in question.

The data above given concerning the phenomena of reduction certainly are in accordance with the generalizations here advanced. The writer makes no claim to have made an exhaustive search of the chemical literature for data upon this subject, but it should be said that the data here given have not been *selected* to prove the views advanced. Everything found that has any bearing upon the point has been mentioned.

IV. The Phenomena of Oxidation.

Applying the same line of reasoning to the phenomena of oxidation, as was applied to the phenomena of reduction, the same variations in the action of acid and alkaline oxidizing agents are to be looked for as occur with acid and alkaline reducing agents. That is, acid groups ortho to an oxidizable group will decrease the action of acid oxidizing agents upon the oxidizable group, and increase the action of alkaline oxidizing agents. Basic groups ortho to an oxidizable group would decrease the action of alkaline oxidizing, and increase the action of acid oxidizing, agents upon the oxidizable group.

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[1] Ber. d. chem. Ges., **29**, 2448.

Groups in the para position would exercise a like but less strong influence, and groups in the meta position would exercise still less influence, and frequently no appreciable influence at all.

These deductions are in close accord with Remsen's law[1] of oxidation which may be stated as follows: The presence of an acid or negative group in the benzene nucleus, ortho to an oxidizable side-chain, protects that side-chain from oxidation with acid oxidizing agents, and apparently[2] renders it more prone to oxidation with alkaline oxidizing agents.

For the vast majority of the cases thus far investigated, this law holds good. The sulphamide group, and the sulphonic acid group have been found in a few cases[3] to act not in accord with this law.[4]

The data obtainable in regard to the action of basic groups, ortho to an oxidizable group, are more meagre since most of the basic groups, such as the NH_2, CH_3, CH_2Cl, etc., themselves suffer change during the process of oxidation.

With regard to the action of the hydroxyl group some data are obtainable.

Jacobsen[4] states that the oxymetaxylene, $C_6H_3CH_3CH_3OH$ (1, 3, 4), when fused with caustic potash gives the oxymetatoluic acid, $C_6H_3CH_3COOHOH$ (1, 3, 4), and that oxyparaxylene, $C_6H_3CH_3OHCH_3$ (1, 3, 4,), under like conditions gives the oxyparatoluic acid, $C_6H_3CH_3OHCOOH$.

Oxymesitylene,[5] $C_6H_2OHCH_3CH_3CH_3$ (1, 2, 4, 6,), upon fusion with caustic potash, gives the acid, $C_6H_2OHCOOH$ CH_3CH_3 (1, 2, 4, 6). From these data, it appears that the hydroxyl group favors the action of alkaline oxidizing agents, and thus corresponds to its action with alkaline reducing agents (see page 136). Unfortunately we have found no data as to the behavior of the hydroxyl group toward acid oxidizing agents. Facts concerning the behavior of the hydroxyl group toward both acid oxidizing agents and acid reducing agents are very much to be desired.

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[1] This Journal, **4**, 143.

[2] *Ibid.*, **8**, 262.

[3] Hall and Remsen: *Ibid.*, **2**, 130; Remsen: *Ibid.*, **8**, 263.

[4] Ber. d. chem. Ges., **11**, 375.

[5] Hall and Remsen: This Journal, **2**, 141.

Concerning the Halogen Elements.

Since the halogen elements when combined with carbon appear to attract acid reagents as shown by the phenomena of substitution already mentioned, and since chlorine, as has been pointed out (page 136) favors the action of acid reducing agents and retards the action of alkaline reducing agents, we should expect it to favor the action of acid oxidizing agents and retard the action of alkaline oxidizing agents, and hence, to stand in direct opposition to Remsen's law. These conclusions, however, do not appear to be altogether in accord with the facts.

Beilstein and Vollrath[1] state that chlormetaxylene, $C_6H_3CH_3CH_3Cl$ (1, 3, 4), when oxidized with chromic acid gives the chlortoluic acid, $C_6H_3COOHCH_3Cl$ (1, 3, 4), indicating that chlorine protects the ortho methyl group.

Trichlormetaxylene, $C_6HCH_3ClCH_3ClCl$ (1, 2, 3, 4, 6), according to Vollrath, resists entirely the oxidizing action of chromic acid and of nitric acid, again showing protection to the ortho methyl group by the chlorine.

Schmitz[2] states that bromine in brommesitylene protects the two ortho methyl groups from oxidation with chromic acid.

The same is true of chlorine in chlormesitylene.[3]

Von Gerichten[4] has shown that chlorcymene, $C_6H_3CH_3ClC_3H_7$ (1, 2, 4), when oxidized with chromic acid gives chlortoluic acid, $C_6H_3CH_3ClCOOH$ (1, 2, 4). This action however may well be due to the general tendency of the propyl group of cymene to suffer oxidation before the methyl group, rather than to any protective action of the chlorine. The isomeric chlorcymene, $C_6H_3CH_3ClC_3H_7$ (1, 3, 4), gave by oxidation an acid, $C_6H_3COOHClC_3H_7$, or $C_6H_3CH_3ClC_2H_4COOH$; von Gerichten himself believed it to be the latter; if it were the former acid the protective power of the chlorine would be clearly shown.

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[1] Ann. Chem. (Liebig), **144**, 266 and 271.

[2] *Ibid.*, **193**, 171; also **147**, 8.

[3] *Ibid.*, **150**, 325.

[4] Ber. d. chem. Ges., **11**, 364 and 1719.

Remsen and Morse[1] find that bromparaethyltoluene, $C_6H_3CH_3BrC_2H_5$ (1, 2, 4), when oxidized with chromic acid, gives bromparatoluic acid, $C_6H_3CH_3BrCOOH$ (1, 2, 4). Here also this may be due to the fact that paraethyltoluene when oxidized gives paratoluic acid and no paraethylbenzoic acid, rather than to any protective influence of the bromine. If the isomeric bromparaethyltoluene, $C_6H_3CH_3BrC_2H_5$ (1, 3, 4), were to give the acid, $C_6H_3COOHBrC_2H_5$ (1, 3, 4), then the protective influence of bromine would be clearly shown.

The facts quoted tend to confirm Remsen's law and to prove false the assumptions made here, nevertheless a few statements have been found that are in accord with these assumptions and apparently in conflict with the facts just quoted.

Fittig[2] states that orthochlortoluene is completely burned up by chromic acid, showing that chlorine intensifies the action of chromic acid.

Noyes[3] has found that both ortho- and parabromtoluene are more difficult to oxidize, than toluene itself with alkaline solution of potassium ferricyanide, and that the ortho compound is more difficult to oxidize than the para compound. Later, Noyes and Walker[4] point out that metabromtoluene is the easiest of the three bromtoluenes to oxidize with alkaline potassium ferricyanide solution,—facts which illustrate the retarding influence of bromine upon alkaline oxidizing agents, and as well the relative influence of the ortho, meta, and para positions according to the assumption here made. Further investigation of the action of the halogen elements toward both acid and alkaline oxidizing agents, and toward acid and alkaline reducing agents are very desirable, in order to learn whether or not these two classes of phenomena show similar variations.

Finally, as regards the actual influence of the meta position, there is much less evidence than for the other positions, but the little evidence obtainable, goes to show that in the meta position, groups have very little influence.

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[1] This JOURNAL, **1**, 138.

[2] Ztschr. Chem., N. F., **7**, 179.

[3] This Journal, **5**, 105.

[4] *Ibid.*, **8**, 186.

Noyes and Moses[1] have shown that metanitrotoluene is much more difficult to oxidize with alkaline potassium ferricyanide than either the ortho- or paranitrotoluene. Upon this point the authors say: "Their conduct seems to indicate that it is not so much that a nitro group in the meta position protects a methyl group, as that a nitro group in the ortho or para position has, as it were, a loosening effect on a methyl group, causing the latter to be more easily attacked by the oxidizing agent which we are studying."

Remsen and Palmer[2] have shown that metatoluenesulphamide is oxidized with equal facility, with both acid and alkaline oxidizing agents.

To repeat, in conclusion, so far as all of the phenomena of the four classes here considered are concerned, it seems to the writer that the Claus formula is better in accord with the actual properties of benzene compounds, than any other benzene formula that has yet been suggested.

Applying the van 't Hoff-LeBel theory to the Claus formula, using tetrahedrons to represent the carbon atoms, we get as the configuration of the benzene molecule,

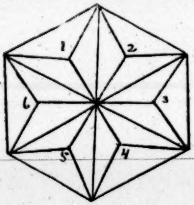

Fig. IV.

or

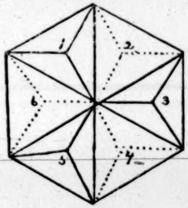

Fig. V.

In the first the apices of the tetrahedrons showing the positions of the hydrogen atoms are all in one plane on the same side of the molecule. In the second the hydrogen atoms lie alternately in two planes, one above and the other below the plane of the carbon atoms. The former of these has been suggested by Loschmidt.[1] Baeyer[2] has also suggested essentially the same configuration in connection with his "centric formula." The second form given above has been suggested by Marsh[3] and by Vaubel.[4]

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[1] This Journal, 7, 149.

[2] *Ibid.*, 4, 142.

Vaubel's chief reason for preferring his formula to that of Loschmidt, is that in it the ortho and the para positions are on the same side of the molecule, and on the opposite side of the molecule from the meta-position. Hence the ortho- and para-positions have properties in common which distinguish them from the meta position. On this point he says[5]: "This configuration shows us that in the formation of ortho and para-derivatives the substituting groups occupy different sides of the molecule. We can in this case assume that the substituting groups exercise a mutually repelling action. When they attract one another, on the contrary, meta derivatives will be obtained, which may be induced by the action of heat or some similar influence to go over into ortho- and para derivatives."

It will be observed that the assumptions here made are the exact reverse of the conclusions set forth in this article, and it appears to the writer that Vaubel's assumptions in this regard are not warranted when the nature of the groups that assume the different relations with respect to each other is taken into consideration. Moreover, in the Vaubel formula groups which are in the ortho position (*e. g.*, the carboxyl groups in phthalic acid) have the fumaroid relation to one another, which we have learned is characterized by the inability to form an anhydride. But the ortho-compounds in the benzene series are just those which best give anhydrides. It appears, therefore, from this point of view, that the Loschmidt formula in which groups in the ortho position have the maleinoid relation is the preferable one.

Again Baeyer has shown that when terephthalic acid is reduced with sodium amalgam two geometrically isomeric $\Delta^{2.5}$

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[1] Monatsh. f. Chem., **11**, 28 (1890).

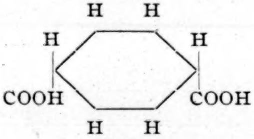
[2] Ann. Chem. (Liebig), **245**, 123.

[3] Phil. Mag., Nov., 1888.

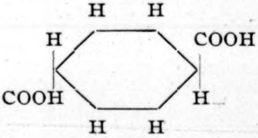
[4] J. prakt. Chem. (2), **44**, 137; **48**, 75, 315; **49**, 308, 540; **50**, 58, 362; **51**, 444; **52**, 417, 548; **53**, 241, 549.

[5] *Ibid.*, **44**, 142.

dihydroterephthalic acids are formed,[1] the maleinoid or cis form and the fumaroid or cistrans form which may be represented by the figures :



Cis form.



Cistrans form.

As the formulas indicate, the cistrans form is, like fumaric acid, the more stable (the carboxyl groups tending to get as far apart as possible), the cis form being changed into the cistrans by heating with hydrochloric acid. Now if the Vaubel formula is correct, simple reduction would give at once the cistrans modification and as this form does not tend to pass over into the cis form we should expect by this simple reduction to get only the cistrans form. The Loschmidt formula would by simple reduction give only the cis modification, but as this tends to pass over into the cistrans modification both modifications would be present in the reduction product unless unusual precautions were taken to prevent the secondary reaction.

Baeyer[1] also concludes that the hexahydromellitic acid obtained by the direct reduction of mellitic acid is the maleinoid form. The Loschmidt formula would account for this, but the Vaubel formula would indicate the formation of the fumaroid hexahydromellitic acid.

In the Loschmidt formula if one of the para bonds is broken the remaining para bonds can rearrange themselves in the form of double bonds with little or no change in the geometrical configuration. Indeed Loschmidt proposed this configuration assuming the three double bonds of the Kekulé formula ; that is, he assumed that carbon atoms 1 : 2, 3 : 4, and 5 : 6 in Fig. IV are connected by double bonds and that carbon atoms 2 : 3, 4 : 5, and 5 : 6, are joined by single bonds.

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[1] Ann. Chem. (Liebig), **251**, 290 and 296.

[1] *Ibid.*, **245**, 134.

This configuration, along with Vaubel's, indicates better than any other configuration the fact that in some cases (as for example with phloroglucin) the three double bonds might be present without essential alteration of the configuration.

If any value whatever can be attached to the suggestions put forth in this paper, it is that they bring together and show an apparent relation between a considerable number of facts which have hitherto been considered as independent phenomena. Their chief merit, however, is the fact that experimental evidence can rapidly be accumulated which will render them much more probable than they now seem; or else will render them wholly untenable.

STANFORD UNIVERSITY, CALIFORNIA,
May 25, 1900.

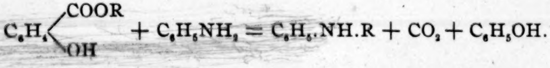
Contributions from the Havemeyer Laboratories of Columbia University.

XXXIX.—THE SYNTHESIS OF AMINES BY THE USE OF ALKYL SALICYLATES.

BY ALFRED TINGLE.

THEORETICAL.

It has been previously shown[1] that when alkyl salicylates are boiled with an excess of aniline, the alkyl group is introduced into the aniline molecule, a secondary amine being produced. The reaction may be expressed by the following equation:



$$C_6H_4\begin{cases}COOR\\OH\end{cases} + C_6H_5NH_2 = C_6H_5.NH.R + CO_2 + C_6H_5OH.$$

It was also shown that when dry ammonia is passed into boiling methylic salicylate, dimethylamine is produced, but no phenol is formed.

In the earlier papers a provisional theory was put forward as to the manner in which the reaction between aniline and methylic salicylate took place. Subsequent investigation has shown that this theory is inadequate.

The work described in the present communication was undertaken mainly in the hope of throwing light on the mechanism of the synthesis.

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[1] This JOURNAL, **24**, 52; **24**, 276–281.

It was in the first place necessary to know precisely what products were formed when dry ammonia reacts with methylic salicylate. The volatile one had been already shown to be dimethylamine. The investigation was therefore in this instance confined to the non-volatile substances which remain dissolved in the excess of methylic salicylate.

By passing ammonia into the boiling ester for twenty hours, a sufficient quantity of these was obtained for investigation. The mixture was separated into its constituents by extraction with hot alcohol, and on cooling the soluble substance crystallized. It melted at 139°, gave a blue-purple color with ferric chloride, and had the same crystalline form as salicylamide, with which it was clearly identical.

The substance insoluble in alcohol was crystallized from benzene. It forms greenish-yellow needles and melts above 280°. Both its appearance and general behavior support the idea that it is polysalicylic nitrile. Limpricht[1] obtained this substance by heating salicylamide to 270°; Miller[2] states that it melts at 296° to 299°. The amount produced in the reaction at present under consideration is quite small.

It may therefore be stated that ammonia acts on methylic salicylate at its boiling-point to produce dimethylaniline and salicylicamide: the latter is then partly converted into polysalicylicnitrile. The non-production of phenol in the reaction seemed a noteworthy point, making it at first difficult to see what mechanism it might have in common with the production of alkylanilines. Further study has, however, removed the difficulty.

The action of dry ammonia gas on ethylic salicylate and on isoamylic salicylate was next studied. These have been shown to act much more slowly upon aniline than does methylic salicylate. When ammonia gas was passed into the esters, at their boiling-point, during four hours, it was found that the reaction had not proceeded to any appreciable extent. The ethylic ester gave a trace of what appeared to be polysalicyl nitrile, but in the case of neither ester was there the slightest evidence of the production of an amine, and the work in this direction was suspended. The velocity of these reactions is clearly decreased by the increasing mass of the alkyl group involved.

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[1] Ann. Chem. (Liebig), **98**, 261.

[2] Ber. d. chem. Ges., **22**, 2798.

The action of aniline on methylic benzoate was next studied. These bodies, after being carefully dried, were boiled together for six and a half hours. Two experiments were made: In one, the substances were present in equimolecular proportions; in the other, an excess of aniline was employed. In both cases the sole product was benzanilide; neither methylaniline nor dimethylaniline was produced. It is also noteworthy that the absence of hygroscopic moisture did not diminish the production of the anilide, as is the case when aniline and methylic salicylate react.

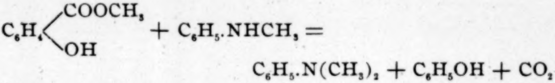
An attempt was next made to see whether the reverse reaction took place. Benzoic acid and dimethylaniline (in the proportion of 4 molecules of the former to 1 of the latter) were boiled together for nine hours. From the resulting mixture a neutral liquid was obtained, which gave, when distilled, methylic benzoate and a small tarry residue. It was not possible to show, in the latter, the presence of either benzanilide or methylbenzanilide. Probably any aniline or methylaniline formed in the reaction would finally appear in that form. Failure to detect their presence may be fairly attributed to the slight amount formed, and to their liability to be converted into resins under the conditions of the experiment. Attempts to show that aniline or methylaniline accompanied the unchanged dimethylaniline were equally unsuccessful.

It seemed to the writer that a basis was now provided on which a complete explanation of the reactions so far studied might rest. It may be supposed that we have to do with a reversible reaction which is represented by the following equations:

$$(1)\ \mathrm{R.COO.R' + C_6H_5.NH_2 = R.COOH + C_6H_5.NHR'};$$
$$(2)\ \mathrm{C_6H_5NHR' + RCOOH = C_6H_5.NH_2 + R.COOR'}.$$

In the case of methylic benzoate and aniline, it would then appear that the velocity of the reaction (1) is much less than that of reaction (2). Thus, supposing the former to occur to any extent, it would be quickly reversed, since the benzoic acid would only be removed slowly from the sphere of activity by conversion into benzanilide. Direct evidence that the reaction (2), or one similar to it, does occur is supplied by the formation of methylic benzoate from benzoic acid and dimethylaniline. When an alkyl salicylate and aniline are boiled together the reaction is practically non-reversible; however slowly that represented by equation (1) takes place, it will be quickly followed by the decomposition of the liberated salicylic acid into carbon dioxide and phenol, and that represented by equation (2) cannot, therefore, take place. The reason for the non-production of phenol when ammonia gas acts on boiling methylic salicylate appears to be that, in the presence of an excess of ammonia, the liberated salicylic acid at once forms ammonium salicylate; this, at the temperature of the experiment, is decomposed into salicylamide and water. Part of the amide then further loses water and forms polysalicylic nitrile. It seems that the different course of the reaction is due to the formation of salicylamide being more rapid, under the conditions of the experiment, than is the formation of phenol.

If, however, this view of the general nature of the reaction is correct, it follows that tertiary amines might also be produced. The reaction



$$C_6H_4\left\langle\begin{matrix}COOCH_3\\OH\end{matrix}\right. + C_6H_5.NHCH_3 = C_6H_5.N(CH_3)_2 + C_6H_5OH + CO_2$$

might take place slowly, but there would be no obvious reason why it should not take place at all.

Hitherto no formation of a tertiary amine by this reaction had been observed. The conditions had, however, always been such as to favor the formation of a secondary amine. In all experiments the base had been in excess of the ester. An experiment was therefore made to determine whether in *all* circumstances secondary amines only are produced. Methylic salicylate and aniline, in the proportion of two molecules of the former to one of the latter, were boiled together for six hours. The resulting basic oil consisted of dimethylaniline, without any trace of either unchanged aniline or of methylaniline.

A further consequence of the theory of this reaction is that other alkyl esters should yield alkylanilines when boiled with aniline, provided that the acid from which they are derived is unstable at the temperature of the experiment. When, however, the acid is stable, we need expect no such reaction to take place, or should it do so, it would be more or less completely reversed. Limpricht[1] showed that when the three hydroxybenzoic acids are distilled with aniline, the ortho and the para acids are almost completely converted into phenol, while the meta acid gives no phenol, but a good yield of *m*-hydroxybenzanilide. From this it follows that esters of *p*-hydroxybenzoic acid should give alkylanilines, but that *m*-hydroxybenzoic esters should not do so.

Methylic *p*-hydroxybenzoate was boiled for four hours with three molecular proportions of aniline. The products were phenol, unchanged ester, aniline, and dimethylaniline. No methylaniline was found. Under the same circumstances (an excess of aniline), the salicylic ester gives phenol and methylaniline.[2] None of the ester remains undecomposed, and no dimethylaniline is formed. We thus see that methylic salicylate reacts more rapidly with aniline than does methylic *p*-hydroxybenzoate, but the production of dimethylaniline by the latter tends to show that methylaniline is more quickly acted upon by it than by methylic salicylate.

Methylic *m*-hydroxybenzoate does not appear to have been hitherto described. It is readily prepared by Fischer's method ; it may be purified by crystallization from a mixture of benzene and light petroleum, and is deposited in bunches of beautiful white needles. Its melting-point is 70°.

Methylic *m*-hydroxybenzoate was boiled for six hours with three molecular proportions of aniline. The non-basic products were unchanged ester and *m*-hydroxybenzanilide. After removing the excess of aniline from the basic products, the residue consisted of a small amount of an oil, which did not yield methylacetanilide when treated with acetyl chloride. It had no constant boiling-point; the larger portion distilled between 230° and 250°. It was not, therefore, dimethylaniline, the boiling-point of which is 191° to 193°. Probably it consisted of the concentrated impurities from the 59 grams of aniline employed; the quantity obtained was too small for further investigation.

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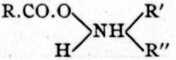
[1] Ber. d. chem. Ges., **22**, 2907.

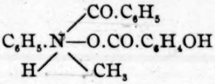
[2] This JOURNAL, **24**, 52.

The facts so far investigated seem, in the main, to lead to the conclusion that the production of amines by salicylic esters merely depends on the rapid removal, under the experimental conditions, of salicylic acid. An analogy is readily seen between the action of alkyl esters and of alkyl haloids on ammonia or on amines. The greater ease with which alkyl haloids react is probably attributable to the facility with which the haloid acid produced in the reaction is neutralized by the formation of stable ammonium salts. Analogy suggests the formation of similar unstable intermediate compounds of the type

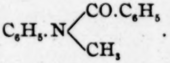


in this synthesis.

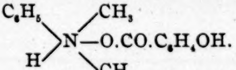
Apart from such analogy, the only evidence bearing upon the point is furnished by the fact that no reaction could be observed when methylic salicylate and benzanilide or isoamylic salicylate and acetanilide were boiled together during five and six hours, respectively. This is readily understandable if it be remembered that the formation of the compound



must precede that of the compound



It is easily seen that the former would be produced with much greater difficulty than would, for example, the compound



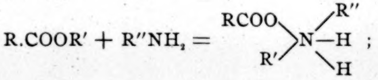
It seems probable, also, that the formation of these substituted ammonium salts precedes the formation of amides and anilides from esters.

It is, at first sight, conceivable that the formation of an anilide from an ester might depend entirely on the presence of traces of water (as was shown to be the case with salicylanilides[1]), and that the water acts by first hydrolyzing the ester. In such case the reaction would be represented as follows:

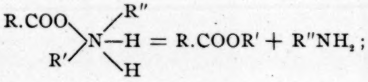
$$\mathrm{R.COOCH_3 + H_2O = R.COOH + CH_3OH;}$$

$$\mathrm{R.COOH + C_6H_5NH_2 = R.CONH.C_6H_5 + H_2O.}$$

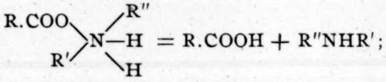
Such an idea is, however, set aside when one sees that dried methylic benzoate and anhydrous aniline give a fair yield of anilide when boiled together in a dry apparatus. On this view the possible actions of an ester on a primary amine would be represented as follows:

(1) 

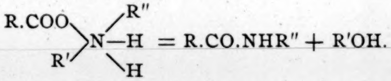
$$\mathrm{R.COOR' + R''NH_2 = \left.\begin{matrix}RCOO\\R'\end{matrix}\right> N \left<\begin{matrix}R''\\H\\H\end{matrix}\right.;}$$

(2) 

$$\mathrm{\left.\begin{matrix}R.COO\\R'\end{matrix}\right> N \left<\begin{matrix}R''\\H\\H\end{matrix}\right. = R.COOR' + R''NH_2;}$$

(3) 

$$\mathrm{\left.\begin{matrix}R.COO\\R'\end{matrix}\right> N \left<\begin{matrix}R''\\H\\H\end{matrix}\right. = R.COOH + R''NHR';}$$

(4) 

$$\mathrm{\left.\begin{matrix}R.COO\\R'\end{matrix}\right> N \left<\begin{matrix}R''\\H\\H\end{matrix}\right. = R.CO.NHR'' + R'OH.}$$

The above general formulæ may obviously be applied to secondary amines, or to ammonia. As soon as reaction (1) has been brought about, it will depend on the nature of the reacting substances, and the experimental conditions, whether reaction (2), (3), or (4) is the predominant one. For example, when dry methylic salicylate and aniline are boiled together, reaction (3) only takes place; when a trace of water is present reaction (4) proceeds to some extent. When dry ammonia acts on boiling methylic salicylate, reaction (3) is still predominant. If the latter substances react at 100° and in the presence of water and alcohol, then reaction (4) is the only one to occur; when methylic benzoate and aniline are boiled together, reactions (2) and (4) predominate.

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[1] This JOURNAL, 24, 52.

EXPERIMENTAL.

Ammonia Gas and Methylic Salicylate.

Dry ammonia was passed into boiling methylic salicylate for about twenty hours. After cooling the liquid, light petroleum was added, and the crystals which separated were filtered off. The greater part of the mother-liquid was then distilled over, and more crystals separated from the residue. These were combined with those previously deposited; the mixture obtained was extracted with hot alcohol and the resulting solution was filtered; crystals deposited from the filtrate when cool, which, by their form, their melting-point (139°), and their behavior towards alcoholic ferric chloride solution, were identified as salicylamide.

That small portion of the mixture which was insoluble in alcohol was dissolved in hot benzene, from which greenish-yellow crystals were deposited on cooling. These melt above 280° and appear to consist of polysalicyl nitrile. This body was obtained by Limpricht,[1] when salicylamide was heated at 270°. According to Miller[2] its melting-point is 296°-299°.

Ammonia Gas and Ethylic Salicylate.

Dry ammonia was passed into boiling ethylic salicylate for about four hours. The escaping gas was collected in water; after neutralizing the solution with hydrochloric acid, no diethylamine or other ethylated ammonia could be discovered. Examination of the residual ester showed only a minute trace of what was probably polysalicyl nitrile (see above).

Ammonia Gas and Isoamylic Salicylate.

An experiment similar to the above was made, using isoamylic salicylate instead of the ethylic ester. No action was observed to have taken place.

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[1] Ann. Chem. (Liebig), **98**, 261.

[2] Ber. d. chem. Ges., **22**, 2798.

Separation of Aniline, Methylaniline, and Dimethylaniline.

In all experiments where this operation was necessary, the method followed was that recommended by A. W. Hofmann.[1] It is briefly described in Beilstein's "Handbuch."[2] The only change introduced was to repeat the treatment of the free bases with dilute sulphuric acid a second, or even a third, time before proceeding to separate the methylaniline and dimethylaniline.

Methylic Benzoate and Aniline.

Methylic benzoate (54.4 grams) was dried over calcium chloride and mixed with an equimolecular proportion of aniline (37.2 grams) which had been dried over sodium. The mixture was boiled for six and a half hours in a dry flask fitted with a reflux condenser. When cool, crystals of benzanilide separated. They melted at 159°, and, when hydrolyzed, gave aniline and benzoic acid. Yield, 8 grams. The filtrate from these crystals was poured into dilute hydrochloric acid and shaken with ether. The latter removed the unchanged methylic benzoate, while all bases were dissolved in the acid liquid. This was then separated, neutralized with sodium hydroxide, and extracted with ether; the ether was distilled off and the residue treated with the object of separating any methylaniline or dimethylaniline formed in the reaction. After removing the aniline only a few drops of oil remained. This became gummy when treated with acetyl chloride, and no methylacetanilide resulted. The amount was too small for further investigation.

It would thus seem that neither methylaniline nor dimethylaniline was formed in this experiment. The residual oil probably consisted of the concentrated impurities originally present in the aniline.

Another experiment, carried out in a similar manner, but using 4.5 molecular proportions of aniline to 1 molecular proportion of methylic benzoate, gave an equally negative result, the products being benzanilide, unchanged ester, and aniline.

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[1] Ber. d. chem. Ges., 10, 599.

[2] 3te Auf., 2ter Band, 324.

Dimethylaniline and Benzoic Acid.

Four molecular proportions (48.8 grams) of benzoic acid and 1 molecular proportion (12 grams) of aniline, were boiled together for nine hours. The product was dissolved in ether, and the solution repeatedly extracted with a solution of potassium carbonate to remove the excess of benzoic acid. The aniline bases were then removed from the ether by extraction with dilute hydrochloric acid. Once more the ethereal liquid was shaken with a solution of potassium carbonate; it was then dried and the ether removed by distillation on the water-bath. The residue was an oil of which there was so little that an accurate determination of its boiling-point could not be made. It passed over, however, between 150° and 200°, leaving only a tarry residue. It did not mix with water or with concentrated hydrochloric acid. It dissolved on warming with a solution of potassium hydroxide in dilute alcohol. This solution was cooled and acidified with hydrochloric acid. Crystals separated which melted at 120°. They gave both the smell and the characteristic crystalline form of benzoic acid when sublimed. On these grounds it is inferred that the liquid from which they were produced was methylic benzoate, the boiling-point of which is 199°. An unsuccessful attempt was made to isolate aniline or methylaniline from the unchanged dimethylaniline, and it was not possible to demonstrate the presence of benzanilide or methylbenzanilide in the tar which accompanied the methylic benzoate.

Methylic Salicylate and Aniline.

Two molecular proportions of methylic salicylate (50 grams) and 1 molecular proportion of aniline (15 grams) were boiled together for six hours. The product was poured into dilute hydrochloric acid, and the phenol removed by shaking with ether. On neutralizing the acid solution, a base separated which was extracted with ether. After removing the ether it was shown, by the dilute sulphuric acid test, to be free from aniline. No methylacetanilide was formed on treating the base with acetyl chloride. It boiled at 192° to 193° (boiling-point of dimethylaniline 191° to 193°). It is evident that, under these circumstances no methylaniline, but only dimethylaniline, is produced. The yield of purified base was 8.3 grams.

Methylic p-Hydroxybenzoate and Aniline.

These substances were boiled together for four hours, 15.2 grams (1 molecule) of ester and 27.9 grams (3 molecules) of aniline being employed. The product was subsequently distilled. A considerable portion of unchanged ester remained in the distilling flask. The distillate was poured into a solution of potassium hydroxide and extracted with ether. The ethereal layer was separated, the ether distilled, and the residue treated with a view to separating the constituent bases. Aniline was, of course, present in excess; no trace of methyl aniline was found, but a quantity of dimethylaniline (boiling at 191°) was isolated. The weight of this substance finally obtained was 2.4 grams, but the true yield was somewhat greater. Through an accident, about a gram of the base was lost after purification, before it could be weighed.

The alkaline liquid, from which the bases were extracted, was acidified and extracted with ether. From this extract phenol and *p*-hydroxybenzoic acid were obtained. The latter doubtless was formed by hydrolysis of that portion of the ester which distilled over. Phenol was, as usual, identified by its smell and by the formation of its tribromderivative.

Methylic m-Hydroxybenzoate and Aniline.

Three molecular proportions (59.2 grams) of aniline were boiled for six hours with 1 molecular proportion (27.9 grams) of methylic *m*-hydroxybenzoate. The product was then distilled, leaving a tarry residue. Bases were extracted from the distillate by dissolving it in ether and shaking with dilute hydrochloric acid. That part remaining dissolved in the ether was found to consist of *m*-hydroxybenzanilide and unchanged methylic *m*-hydroxybenzoate; no phenol could be detected. The acid solution was made alkaline and the free bases extracted with ether. Aniline was separated in the usual manner.

Acetyl chloride and water caused no precipitation of methylacetanilide. On the addition of alkali a few drops of an oil separated. It was extracted with ether and carefully examined, but did not appear at all similar to dimethylaniline. It did not possess a constant boiling-point, but the greater part boiled between 230° and 250°. The quantity obtained was, however, so small that these points even are uncertain. It seems probable that it is a mixture of impurities originally present in the aniline.

Methylic m-Hydroxybenzoate.

This compound appears not to have been hitherto described. It is readily prepared by Fischer's esterification method, using the same concentration of sulphuric acid in methyl alcohol as for the preparation of methylic salicylate. The yield is very good. The ester is readily purified by crystallization from a mixture of benzene and light petroleum. It forms clusters of magnificent long, white needles, and melts at 70°.

Methylic Salicylate and Benzanilide.

These substances were boiled together for five hours, in the proportion of 2 molecules of the former to 1 of the latter. The mixture was subsequently hydrolyzed by boiling with a solution of potassium hydroxide. Aniline was liberated, but no methylaniline could be detected, thus showing that no methylbenzanilide had been formed.

Isoamylic Salicylate and Acetanilide.

Two molecular proportions of isoamylic salicylate and 1 molecular proportion of acetanilide were boiled together for six hours. The product was treated as in the preceding experiment. The result showed that no isoamylacetanilide had been formed.

Methylic Salicylate and Ammonia in the Presence of Dilute Alcohol.

Several grams of methylic salicylate were mixed with an excess of strong aqueous ammonia (sp. gr. 0.9), and sufficient alcohol to dissolve the ester. The mixture was heated in a pressure bottle, at 100°, for three hours. After cooling, the product was acidified, and the salicylamide was extracted with ether. On evaporating the aqueous layer, ammonium chloride separated, but no methyl derivative could be detected.

HAVEMEYER HALL,
COLUMBIA UNIVERSITY.

NOTES.

Argon and Its Companions.

Following is an abstract of a paper by William Ramsay and Morris W. Travers, read before the Royal Society, November 15, 1900, and published in the Chemical News of November 30:

The discovery of krypton and neon was announced to the Royal Society in the early summer of 1898; and, subsequently, atmospheric air was found to contain a heavier gas to which the name of xenon was applied. Mr. Baly, in the autumn of the same year, called attention to the presence of helium lines in the spectrum of neon, an observation which confirms that made by Professor Kayser, of Bonn, and by Dr. Friedländer, of Berlin.

At the same time we imagined we had obtained a gas with a spectrum differing from that of argon, and yet of approximately the same density. To this gas we gave the name metargon. It has now been found that the presence of the so-called metargon is to be accounted for by the fact that in removing oxygen from the mixture of these gases, which was then in our hands, phosphorus containing carbon was employed; this mixture, when burned in oxygen, yields a spectrum to some extent identical with that furnished by carbon monoxide, but differing from it inasmuch as lines of cyanogen are also present. We have no doubt that the so-called metargon, the spectrum of which is visible only at high pressure, and only when impure phosphorus has been employed to remove oxygen, must be attributed to some carbon compound. In spite of numerous experiments we have not yet succeeded in producing any gas in quantity which yields this composite spectrum. It is only to be obtained by a mixture of carbon monoxide with cyanogen.

To obtain the heavier gases, krypton and xenon, a large amount of air was allowed to evaporate quietly; the residue was freed from oxygen and nitrogen, and then consisted of a mixture of krypton, xenon, and argon, the last forming by far the largest portion of the gas; this mixture was liquefied by causing it to flow into a bulb immersed in liquid air, and the bulk of the argon was removed as soon as the temperature rose, the krypton and the xenon being left behind. By many repetitions of this process we were finally successful in separating these three gases from each other. While krypton has a considerable vapor-pressure at the temperature of boiling air, the vapor-pressure of xenon is hardly appreciable, and this afforded a means of finally separating these two gases from one another; in the complete paper the operations necessary to separate them are fully described.

For neon the process of preparation was different. The air liquefier furnished a supply of liquid air; the gas escaping from the liquefier consisted largely of nitrogen; this mixture was liquefied in a bulb immersed in the liquid air which the machine was making. When the bulb had been filled with liquid nitrogen a current of air was blown through the liquid until some of the gas had evaporated. That gas was collected separately, and deprived of oxygen by passage over red-hot copper; it contained the main portion of the neon and the helium present in the air. The remainder of the nitrogen was added to the liquid air used for cooling the bulb in which the nitrogen was condensed. Having obtained a considerable quantity of this light nitrogen it was purified from that gas in the usual manner, and the argon containing helium and neon was liquefied. By fractional distillation it was possible to remove the greater portion of the helium and neon from this mixture of gases, leaving the argon behind. Many attempts were made to separate the helium from the neon. Among these was fractional solution in oxygen, followed by a systematic diffusion of the two gases; but it was not found possible to raise the density of the neon beyond the number 9.16, and its spectrum still showed helium lines. It was not until liquid hydrogen, made by an apparatus designed and built by one of us (M. W. T.), had been produced in quantity, that the separation was effected; the neon was liquefied, or perhaps solidified, at the temperature of boiling hydrogen, while the helium remained gaseous. A few fractionations served to produce pure neon; we did not attempt to separate the helium in a pure state from this mixture.

That these are all monatomic gases was proved by determination of the ratio of their specific heats by Kundt's method. The physical properties which we have determined are the refractivities, the densities, the compressibilities at two temperatures, and of argon, krypton, and xenon the vapor-pressures and the volumes of the liquids at their boiling-points.

The results are shown in the table on next page.

The compressibilities of these gases also show interesting features. They were measured at two temperatures, 11°.2 and 237°.3; the value of P V for an ideal and perfect gas at 11°.2 is 17,710 meter-cubic centimeters, and at 237°.3 it is 51,800. This is, of course, on the assumption that the prod-

	Helium.	Neon.	Argon.	Krypton.	Xenon.
Refractivities (Air = 1)	0.1238	0.2345	0.968	1.449	2.364
Densities of gases (O=16)	1.98	9.97	19.96	40.88	64
Boiling-points at 760 mm.	?	?	86°.9 abs.	121°.33 abs.	163°.9 abs.
Critical temperatures	?	Below 68° abs.	155°.6 abs.	210°.5 abs.	287°.7 abs.
Critical pressures	?	?	40.2 meters	41.24 meters	43.5 meters
Vapor-pressure ratio	?	?	0.0350	0.0467	0.0675
Weight of 1 cc. of liquid	?	?	1.212 grams	2.155 grams	3.52 grams
Molecular volumes	?	?	32.92	37.84	36.40

uct remains constant whatever be the variation in pressure. Now with hydrogen at 11°.2 C. the product increases with the rise of pressure; with nitrogen, according to Amagat, it first decreases slightly and then increases slightly. With helium the increase is more rapid than with hydrogen; with argon there is first a considerable decrease, followed at very high pressures by a gentle increase, although the product does not reach the theoretical value at 100 atmospheres' pressure; with krypton the change with rise of pressure is a still more marked decrease, and with xenon the decrease is very sudden. At the higher temperature the results are more difficult to interpret; while nitrogen maintains its nearly constant value for P V, helium decreases rapidly, then increases, and the same peculiarity is to be remarked with the other gases, although they do not give the product of P V coinciding with that calculable by assuming that the increase of P V is proportional to the rise of absolute temperature.

That the gases form a series in the periodic table, between that of fluorine and that of sodium, is proved by three lines of argument:

(1) The ratio between their specific heats at constant pressure and constant volumes is 1.66.

(2) If the densities be regarded as identical with the atomic weights, as in the case with diatomic gases, such as hydrogen oxygen, and nitrogen, there is no place for these elements in the periodic table.

The group of elements which includes them is:

Hydrogen	Helium	Lithium	Beryllium
1	4	7	9.
Fluorine	Neon	Sodium	Magnesium
18	20	23	24
Chlorine	Argon	Potassium	Calcium
35·5	40	39	40
Bromine	Krypton	Rubidium	Strontium
80	82	85	87
Iodine	Xenon	Caesium	Barium
127	128	133	137

(For arguments in favor of placing hydrogen at the head of the fluorine group of elements, see Orme Masson, Chemical News, 1896, Vol. **73**, p. 283.)

(3) These elements exhibit gradations in properties such as refractive index, atomic volume, melting-point, and boiling-point, which find a fitting place on diagrams showing such periodic relations. Some of these diagrams are reproduced in the original paper. Thus the refractive equivalents are

found at the lower apices of the descending curves; the atomic volumes, on the ascending branches, in appropriate positions; and the melting- and boiling-points, like the refractivities, occupy positions at the lower apices.

Although, however, such regularity is to be noticed, similar to that which is found with other elements, we had entertained hopes that the simple nature of the molecules of the inactive gases might have thrown light on the puzzling incongruities of the periodic table; that hope has been disappointed. We have not been able to predict accurately any one of the properties of one of these gases from a knowledge of those of the others; an approximate guess is all that can be made. The conundrum of the periodic table has yet to be solved.

The Liquefaction of Hydrogen.

At a meeting of the Physical Society of London, a paper on the above subject was read by Dr. M. W. Travers. An abstract of the paper is given herewith:

These experiments were undertaken in order to provide liquid hydrogen in sufficient quantity for the separation of neon from the helium with which it is usually mixed. The separation is effected by cooling the gases to the temperature of hydrogen boiling at atmospheric pressure. The principles and conclusions do not differ from those of Dewar, but as the production of liquid hydrogen is neither difficult nor costly, an account of the experiments is given.

In 1884, Wroblewski showed that strongly cooled and compressed hydrogen, on being allowed to expand, formed mist or spray in the tube; and, later, Olszewski repeated these experiments on a larger scale, and determined the temperature of the liquid. Other methods of liquefying hydrogen have been suggested by Lord Rayleigh and Kammerlingh Onnes. In the case of many gases a fall of temperature takes place on free expansion, but under ordinary circumstances the temperature rises in the case of hydrogen and helium. The principle of free expansion was first applied by Hampson and Linde to the liquefaction of air. Within the last two years Dewar has shown that at a temperature close to —200° C. hydrogen behaves as an imperfect gas, and becomes cool when allowed to expand. This principle has been applied by Dewar to the liquefaction of hydrogen in quantity. In the author's experiments, hydrogen, under a pressure of 200 atmospheres, passes through a coil which is cooled to —80° C. by a mixture of solid carbonic acid and alcohol. It then enters another coil contained in a chamber which is continually replenished with liquid air. The lower portion of the coil passes into another chamber, which is closed and communicates through a pipe with an exhaust pump. Liquid air flows continuously from the first chamber into the second through a pin valve controlled by a lever. The liquid air, boiling under a pressure of 100 mm. of mercury, lowers the temperature to —200° C. The gas then passes into a regenerator coil, which is enclosed in a vacuum vessel, and, expanding at a valve, passes upwards, through the interstices of the coil and the annular space surrounding the chambers through which the gas first passes, to an outlet whence it can return to the main supply pipe. The liquid which separates from the gas is ultimately collected in a vacuum vessel.

The apparatus, with the exception of the compressor, motor, and Hampson air liquefier, is comparatively inexpensive. About $250 is required for the additional apparatus, and each time liquid hydrogen is made involves a further expenditure of about $5.00.

Centenary Commemoration Lecture at the Royal Institute of Great Britain.

The Centenary Lecture was given by Professor Dewar last June, and has recently been published. The lecturer showed a large number of extremely interesting experiments, and some account of these is given in the abstract herewith communicated:

This large spherical double-walled and silvered vacuum vessel contains 1 liter of liquid hydrogen. You observe it is lifted out of a large cylindrical vessel full of liquid air. In order to diminish the rate of evaporation it is necessary to surround the vessel in which the hydrogen is collected with liquid air. Under such conditions the rapidity of evaporation is about the same as that of liquid air when kept in a similar vessel in the ordinary way. In order to prove that hydrogen is present in the liquid form, the simplest experiment is to remove the cotton-wool plug which takes the place of a cork, and insert a metallic wire, to the end of which is attached a ball of asbestos for the purpose of absorbing the liquid. On bringing it quickly into the air and applying a light, it burns with the characteristic appearance of the hydrogen flame. The liquid can readily be poured from one variety of vacuum vessel into another, so that by means of this unsilvered cylindrical form the appearance of the liquid and other experiments may be projected on a screen. The liquid hydrogen appears in gentle ebullition and is perfectly clear, only there is a white solid deposit in the bottom of the tube, which is really solid air. This may be shown by removing for an instant the cotton-wool stopper, when you see a snow of solid air falling in the liquid. It is easy to arrange a method of carrying liquid hydrogen in a small vacuum vessel in such a way as to prevent the access of air. For this purpose the vacuum vessel, after it has been filled by dipping it into the main supply by means of a supporting wire, is surrounded with a glass envelope, which becomes filled with an atmosphere of hydrogen gas constantly maintained, thereby preventing the access of air. That the density of the liquid is very small and is altogether unlike liquid air is shown by dropping small pieces of cork, which float readily in the latter liquid, but sink instantly in the hydrogen. The real density of the liquid is only 1/14 that of water, so that it is by far the lightest known liquid. This small density explains the rapidity with which the liquid is cleared on the entrance of the air snow. The relative smallness of the gas bubbles produced in the actively-boiling liquid which causes an appearance of opalescence, is really due to the small surface-tension of the liquid hydrogen. The coefficient of expansion of liquid hydrogen is some five times greater than that of liquid oxygen, and is comparable with that of carbonic acid, about 5° from its critical point. The latent heat of evaporation is about 190 units, and the specific heat of the liquid is very high, and so far as my experiments go, leads me to the value 6. This is in very marked contrast to the specific heat of liquid oxygen, which is about 0.5. The extraordinary lowness of its boiling-point is at once apparent by cooling a piece of metal in the liquid and then removing it into the air, when it will be seen to condense for a moment solid air on its surface which soon melts and falls as liquid air. This may be collected in a small cup, and the production of oxygen demonstrated by the ignition of a red-hot splinter of wood after the chief portion of the nitrogen has evaporated. If a long piece of quill tubing sealed at one end, but open at the other, is placed in the liquid, then the part that is cooled rapidly fills with liquid air. On stopping any further entrance of air by closing the end of the tube, the liquid air quickly becomes solid, showing in the interior a hollow spindle from contraction, in passing from the liquid into the solid form. On bringing the tube containing the solid from the liquid hydrogen-bath into the air, we observe liquid air running from the surface while the solid air inside is seen to melt. Here is a tube into which liquid oxygen has been poured. On placing it in liquid hydrogen it freezes to a clear blue ice. Liquid nitrogen under similar circumstances forms a colorless ice. If instead of an open tube in free air we employ a closed vessel of about 1 liter capacity to which the quill tube is attached, then, on repeating the experiment, the same results follow, only the volume of the liquid air formed agrees with the total quantity present in the vessel. This suggests that any left in the closed vessel must have a very small pressure. This is confirmed by attaching a mercurial gauge to any vessel containing air, when it will be seen the vacuum produced by hydrogen cooling is equal to that of a Torricellian vacuum. To read such a high exhaustion the solid oxygen and nitrogen, at the boiling-point of hydrogen, must be practically non-volatile or have an exceedingly small vapor-pressure. If the ordinary air contains free hydrogen, helium, etc., which are non-condensable in this way of working, then the vacuum would not be so high as with pure oxygen or nitrogen. This method may be used to separate the incondensable gases from the air. Such air vacua, when examined spectroscopically, show the lines of hydrogen, helium, and neon. We may now employ this process to produce high vacua, and test their exhaustion by the character of the electric discharge. Vacuum tubes which have been prepared in this way show extraordinary resistance to the passage of the electric discharge; they also show the marked phosphorescence of the glass, characteristic of Crookes' tubes. It is, however, the rapidity with which such high exhaustions can be attained that is so interesting. You will observe that this large Geissler tube, previously exhausted to some 3 inches' pressure, will, when the end part is immersed in liquid hydrogen, pass through all the well-known changes in the phases of striation—the glow on the poles; the phosphorescence of the glass—in the space of a fraction of a minute. From this it follows that theoretically we need not exhaust the air out of our double-walled vessel when liquid hydrogen has to be stored or collected. This makes a striking contrast to the behavior of liquid air under similar circumstances. The rapid exhaustion caused by the solidification of the air on the surface of a double-walled unexhausted test-tube, when liquid hydrogen is placed in it, may be shown in another way. Leave a little mercury in the vessel containing air, just as if it had been left from making a mercurial vacuum. Now we know mercury, in such a vacuum, can easily be made to distil at the ordinary temperature when we cool a part of the vessel with liquid air, so that we should expect the mercury in the unexhausted test-tube to distil on to the surface cooled with the liquid hydrogen. This actually takes place. A rough comparison of the relative temperatures of boiling hydrogen and oxygen may be made by placing two, nearly identical, hydrogen gas thermometers operating at constant pressure side by side and cooling each with one of the liquids. It will be seen that the contraction in the thermometer, cooled with liquid hydrogen, elevates the liquid some six times higher than that of the corresponding liquid column of the thermometer placed in the liquid oxygen. A constant-volume hydrogen thermometer gave the boiling-point of 21° absolute or 252° C., and a similar helium thermometer gave the same result. The critical temperature is about 32° absolute or —241° C., and the critical pressure about 15 atmospheres. If a closed vessel is full of hydrogen gas at atmospheric pressure, then, unlike the air vessels, it shows no condensation when a part of it is cooled in liquid hydrogen. To produce liquefaction we must increase the pressure of the gas, or reduce the boiling-point of the liquid hydrogen by exhaustion. Pure hydrogen liquefied in a closed vessel is perfectly clear, showing no trace of color or any appearance of absorption bands in the position of the spectrum lines. Electric sparks passing in the liquid when examined with the spectroscope show the ordinary line spectrum without any reversals. The vapor of boiling hydrogen is about fifteen times denser than that of the ordinary gas, thus bringing it up to the density of air. The liquid hydrogen, at its boiling-point, is about sixty times denser than the vapor coming off. In the case of oxygen the density of the liquid is 255 times that of the vapor at its boiling-point.

If a piece of cotton wool in the form of a little ball is attached to a thread, placed in liquid hydrogen, and then brought into the magnetic field, it is found to be strongly magnetic. This is simply due to the condensation of solid and liquid air in the pores of the wool. This substance we know is magnetic on account of the oxygen it contains. Pure liquid hydrogen is not magnetic, but when the solid air snow is in suspension in the fluid, then the magnetic character of the latter becomes apparent when the vessel is placed in the magnetic field.

All the phosphorescent effects produced at low temperatures formerly described are intensified at the much lower temperature of boiling hydrogen. To stimulate phosphorescence at the temperature of liquid air, ultra-violet light had to be employed, and then the solid body, organic or inorganic, allowed to rise in temperature. It was during the rise of temperature that the marked luminous emission took place. Among inorganic bodies the platinocyanide of ammonia is very remarkable in this respect, and generally the group in organic chemistry known as the ketonic bodies. In the case of bodies cooled in liquid hydrogen, it appears that some show phosphorescence by simple stimulation with the light coming from an ordinary carbon filament electric lamp. The light in this case coming through glass contains only, we may say, the visible spectra, so that the ultra-violet rays are not now essential. It is strange to find photographic action still relatively considerable. At the boiling-point of liquid air the photographic intensity is reduced by 80 per cent of the value at the ordinary temperature. The photographic effect on a sensitive film immersed in liquid hydrogen as compared with the same placed in liquid air is as 1 : 2, so that 10 per cent of the action at ordinary temperatures still remains. As every kind of chemical action so far examined is non-existent at this extreme temperature, these experiments suggest that the cause of the photographic action may be essentially physical. No better illustration could be given of the rapid diminution of chemical action at low temperatures than to remind you that fluorine gas, the most active elementary body, under such conditions, may be liquefied and kept in glass vessels.

The effect of a temperature of 21° absolute on the electric resistance of the pure metals is a problem of great interest. In passing from the melting-point of ice to the boiling-point of hydrogen, pure platinum loses resistance till only 1/40 remains, and in the case of electrolytic copper the remaining resistance is only 1/57 of what it was at starting. Such results suggest the approach to the condition of what may be called relatively perfect electric conductivity as the zero of absolute temperature is approached.

Liquid hydrogen is a non-conductor of electricity, and as regards being an insulator for currents of high potential, it is comparable to that of liquid air. The properties of the liquid we have witnessed in no way suggest the metallic character that chemists like Faraday, Dumas, and Graham anticipated ; and, for the future, hydrogen must be classed with the nonmetallic elements.

The liquefaction of hydrogen has been the consequence of some ten years' devotion to low temperature research. To many it may seem that the results have been indeed costly in more ways than one. The scientific worker who prepares the way for future development in this sort of inquiry generally selects complicated methods, and is attracted or diverted into many by-paths of investigation. He may leave to his successors any credit that may be attached to cheapness and ease of production of the agent of research—results that must invariably follow. Liquid hydrogen is an agent of research which will enable us to examine into the properties of matter at the lowest-maintained temperature ever reached by man. Much work has still to be accomplished. One of the most fascinating problems of the study of low temperatures has been materially advanced. The intervals separating us from the zero of absolute temperature has been reduced to practically 1/4 the value that it stood at when liquid air was the cooling agent. We can produce in pure helium instantaneous temperatures bringing us still nearer the goal. Now we can maintain a temperature within less than 16° of this zero, and the investigator who will make the further attempt to reduce this distance by an equivalent amount, thereby reaching a steady temperature of 4° or 5° absolute, will indeed face a problem of almost insuperable difficulty. Well, let us take comfort in an aphorism of Davy's: "Fortunately for the active and progressive nature of the human mind, even experimental research is only a method of approximation to truth."

Fluosilicic Acid as a Preservative of Manure.

In a recent number of the Chemiker-Zeitung[1] there is an interesting article upon the use of the fluorine compounds formed during the manufacture of superphosphates, which suggest an historical analogy with another member of the same group. In the early days of the LeBlanc process for the manufacture of soda, the hydrochloric acid was allowed to escape until its injurious effects necessitated the passage of laws compelling its removal from the waste gases. This led to the collection and more general use of the acid until finally the profits of the soda industry were all derived from this former waste product. Similar action has recently been taken in Germany to prevent the liberation of injurious amounts of fluorine compounds, which are generated in the manufacture of the fertilizers, and escape through the chimney. These gases are now passed through a series of wooden chambers in which the gases are exposed to a spray of water, which converts the fluorine compounds into silicic and fluosilicic acids. The latter can be separated and converted into its sodium salt, but no use can be made of large quantities of this compound though the aluminium and magnesium salts have been used to harden limestone and sandstone. It has recently been shown that the fluosilicic acid is a better preservative of manure than gypsum and some other substances, in preventing the loss of nitrogen through its influence on the denitrifying agent. This has led to the introduction of a mixture which will generate the acid slowly when applied to the moist manure. Two substances are used in the preparation of this mixture: one, fuller's earth and similar substances mixed with as much sulphuric acid as can be used without destroying the powdery nature of the substance; the other, a solution of the fluosilicic acid treated with enough dried and ground clay to convert the acid into stable salts. Equal parts of the preparations when mixed and sprinkled over the manure generate the fluosilicic acid.

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[1] Chem. Ztg., **75**, 795 (1900).

In place of the sulphuric acid, powdered bisulphate might be used and, in place of the saturated clay a powder formed by passing the gases over lime in order to convert the acid into salts. On account of the price of the preparation its successful use on a commercial scale is as yet an open question.

J. E. G.

Ammonium Bromide and the Atomic Weight of Nitrogen.

During a research having for its chief aim the determination of the hydrogen to oxygen ratio by comparing the equivalents of hydrazine, ammonia, and hydroxylamine, A. Scott[1] found that he could not obtain the same equivalent as Stas for ammonium bromide. The value given by Stas is 98.032, while that of the author is 97.996, his highest value being 98.003. This would lower the atomic weight of nitrogen from 14.046 to 14.010, a number much nearer that deduced from the relative densities of oxygen and nitrogen (16 : 14.003).

The bromide used by Stas seems to have contained some impurity, probably platinum, as it turned grayish at 115°, and its grayness increased up to 180°. He was unable to sublime it even in ammonia without its becoming yellow. The ammonium bromide of the author retains its whiteness at 180° and has been sublimed in ammonia, in a mixture of hydrogen with ammonia and in a vacuum, giving the same results before and after sublimation. The silver bromide had the same composition as that of Stas (57.445 per cent of silver).

The equivalent for ammonium chloride was also determined, and found to be 53.516, as against 53.532 (Stas) and 53.486 (Marignac).

The silver used was prepared by the reduction of silver nitrate by means of ammonium formate, and was notably better than a sample prepared with the utmost care by the well-known cuprous ammonium sulphite process.

To test the purity of the silver in the severest way, the precipitated silver bromide was reduced by hydrogen, when identical results were obtained with the silver so prepared.

Asymmetric Optically Active Sulphur Compounds.

Pope and Peachey have shown that nitrogen and tin compounds, with asymmetric nitrogen and tin atoms respectively, possess optical activity which is to be referred to such asymmetry.

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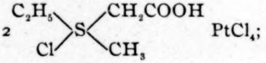
[1] Proceedings of the Chemical Society (London), **16**, 229.

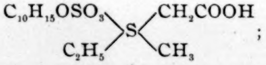
In the case of sulphur compounds many unsuccessful attempts have been made to arrive at the space relations of the groups in sulphonium compounds. The authors mentioned above were unsuccessful in their first attempts to obtain optically active sulphonium compounds. But they found later that they could obtain an optically active double chloride with platinum the formula of which is given below, and besides this they have been able to obtain two other optically active sulphur compounds of the general formula SX_4 which they say are comparable with optically active carbon compounds. In these sulphur compounds, as in the carbon compounds, they consider the sulphur atom to be at the center of a tetrahedron, and the four different groups situated at the apexes. The following formulas represent the three optically active sulphur compounds investigated by these workers:

d-Methylethylthetine platinichloride,



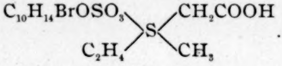
$$2\ \begin{matrix} C_2H_5 & & CH_2COOH \\ & S & \\ Cl & & CH_3 \end{matrix}\ PtCl_4;$$

d-methylethylthetine *d*-camphorsulphonate,



$$\begin{matrix} C_{10}H_{15}OSO_3 & & CH_2COOH \\ & S & \\ C_2H_5 & & CH_3 \end{matrix}\ ;$$

d-methylethylthetine *d*-bromcamphorsulphonate,



$$\begin{matrix} C_{10}H_{14}BrOSO_3 & & CH_2COOH \\ & S & \\ C_2H_4 & & CH_3 \end{matrix}\ .$$

J. C. W. F.

REVIEWS.

DIE AETHERISCHEN OELE, VON E. GILDEMEISTER UND FR. HOFFMANN, Bearbeitet im Auftrage der Firma Schimmel & Co., in Leipzig. Berlin: Julius Springer, 1899. 919 pp.

THE VOLATILE OILS, BY E. GILDEMEISTER AND FR. HOFFMANN, Authorized translation by EDWARD KREMERS. Milwaukee: Pharmaceutical Review Pub. Co., 1900. 733 pp.

Dr. Hoffmann is well-known in this country as the former editor of the Pharmaceutical Review, then Die Pharmaceutische Rundschau. From his pen has come the historical introduction, the history of the volatile oils and of the crude materials, and especially the description of the methods used in obtaining American products. The historical introduction includes a history of the spice trade in antiquity and during the middle ages, a history of the volatile oils, and a history of distillation. The last topic is illustrated by many quaint old illustrations, as well as by cuts showing the forms of apparatus used in large modern establishments.

In the second part of the work are considered, the theoretical basis for obtaining oils by fractional distillation, the more commonly occurring constituents, and general methods of examination. The second of these topics includes a very excellent account of the practical results obtained by Wallach, Semmler, Tiemann, Baeyer, Wagner, Kremers, and others in this field, which is one of the most difficult in organic chemistry.

The remainder of the book, including two-thirds of the whole, is given to a consideration of individual oils, of which 422 are included in the original, and 430 in the translation. This portion of the book has been greatly increased in value by the fact that the authors had at their disposal the observations made in the laboratory of Schimmel and Co., during a long series of years. The authors have also shown excellent judgment in the selection of those facts which will be of value to the chemist who is interested in pure science, to the manufacturer who is interested in methods of production, and to the dealer who is interested in questions of adulteration.

The German edition is magnificently bound in half morocco and well printed on heavy paper. The translation is also well printed and bound, and both editions are embellished with four colored maps and numerous illustrations.

Dr. Kremers has not only rendered the book into clear and idiomatic English but his studies with Wallach, and his own researches in this field have fitted him to act as an editor as well, and in several places results which have appeared since the publication of the German edition are included in the translation. The historical portion has been slightly condensed but the loss has been more than compensated by the bibliographical notes added at the close. W. A. N.

A HANDBOOK OF INDUSTRIAL ORGANIC CHEMISTRY, adapted for the use of Manufacturers, Chemists, and all interested in the utilization of Organic Materials in the Industrial Arts. By SAMUEL P. SADTLER, PH.D., F.C.S., Consulting Chemist, Professor of Chemistry in the Philadelphia College of Pharmacy and in the Franklin Institute of the State of Pennsylvania, etc. Third revised and enlarged edition. Philadelphia: J. B. Lippincott Company. 1900. pp. xviii + 543.

This work appears in substantially the same form as in the second edition, of 1895, but has undergone revision, involving some omissions and rather more considerable additions. Thus, notice is introduced of the treatment of cottonseed and other non-drying or half-drying oils by blowing air through them, to increase viscosity and improve them as lubricants; and, in the chapter on artificial dye-stuffs, a number of the newer dyes are noticed which did not appear in the earlier editions. The general arrangement is based on the raw materials used, instead of on the finished products and their applications. This has some decided advantages, but leads also to some difficulties and anomalies. Thus, most of the little said about explosives is connected on to the fats and oils through nitroglycerin, while gun-cotton is treated in a different part of the book under the head of vegetable textile fibers, and picric acid, the manufacture of which is briefly noticed in the chapter on dye-stuffs, is referred to as an explosive at the end of the section on nitroglycerin, while there is no mention of fulminating mercury or of nitrobenzene as an ingredient of "rend-rock." While, under the head of products obtained by destructive distillation, acetic acid is described, as also in connection with fermentation industries (as vinegar), no account is given of the manufacture of oxalic, tartaric, or citric acid. More space might very well have been given to the rapidly growing industry of more or less "synthetic" perfumes, and the artificial production of such interesting substances as vanillin and coumarin might have been described. Pains have been taken to bring up the statistics of production and importation to more recent years as far as returns are available. The general arrangement of each chapter is clear and likely to be useful to the student, the main headings being Raw Materials, Processes of Manufacture, Products, Analytical Tests and Methods, Bibliography, and Statistics.

J. W. M.

DIE GLYKOSIDE. Chemische Monographie der Pflanzenglykoside nebst systematischer Darstellung der künstlichen Glykoside. Von DR. J. J. L. VAN RIJN, Direktor der landwirtschaftlichen Reichsversuchsstation in Mastricht, Holland. Berlin: Verlag von Gebrüder Borntraeger. 1900. pp. xvi + 511.

The author has attempted to bring together into a condensed form the literature of the glucosides, which is scattered throughout a large number of journals, many of which are not within the reach of most chemists. Until this book appeared the best general account of the glucosides was probably that by O. Jacobsen in Ladenburg's "Handwörterbuch der Chemie," but much work has been done in this field of chemistry since this appeared. The first part of the book deals with the artificial glucosides. After a general discussion of the subject, a detailed description is given of the methods of preparation, properties, and reactions of the compounds of the sugars with alcohols, mercaptans, phenols, aldehydes, ketones, oxyacids, and amines. In the second part the natural glucosides are treated. The material has been arranged according to a botanical classification. The methods for the preparation of the compounds in a pure condition, and their reactions and transformations are given in full. When the chemical structure of the glucoside is known it is given together with the structure of the compounds formed by hydrolysis and other decompositions. While the descriptions of the glucosides are complete in all cases, a number of their synthetical derivatives frequently receive but mere mention. The introduction of the melting-points, boiling-points, solubilities, etc., of these substances would have increased the value of the book. No attempt has been made to give a complete bibliography of the subject, but the more important references are given. In addition to a subject index there is an index of the botanical names used throughout the book. The recently published work is described in an appendix which contains references to papers published as late as 1900. The author has succeeded in preparing a book which will no doubt prove of value to chemists, as it is well written and appears to be accurate. The typography and paper of the book, and the general arrangement of the subject-matter are admirable.

J. F. N.

AN OUTLINE OF THE THEORY OF THERMODYNAMICS. BY EDWARD BUCKINGHAM. New York: The Macmillan Company.

As the author notes in his preface, he has intended this volume of 200 pages to be a brief outline of the "Theory of Thermodynamics," but not to give more applications than are essential in making the subject-matter clear. It is his intention mainly to fill the gap in thermodynamics between the elementary treatment in college text-books and the modern memoirs which have appeared in recent years, particularly from Gibbs and Duhem. In this attempt the author has been most successful. He begins with an elementary, yet most satisfactory, treatment of thermometry and calorimetry, and a general discussion of the variables to be used in the subject. He then proceeds to discuss the first principles of thermodynamics, applying it to some simple problems of thermochemistry and to the ordinary calorimetric properties of fluid. He then discusses the second law of thermodynamics and gives several satisfactory applications to such problems as the electromotive force of a reversible galvanic cell, the changes of state of a single substance, change of osmotic pressure with the temperature, and so on. The next chapter is devoted to the criterion of equilibrium of thermodynamic conditions, in which the author pays particular attention to the necessity of making a new assumption rather than as trying to deduce the criterion from the first two principles. The next chapter deals with thermodynamic potentials and free energy; and in the closing chapter there is found a remarkably clear statement and explanation of the simplest cases of the phase rule.

The whole book is noteworthy for its clearness of treatment and the successful attempt by the author to distinguish between the facts of experiment and the assumptions made in their explanations. One feels at times that too much space is devoted to simple mathematical processes; but, as the book is intended for students who are not as familiar as they might be with elementary mathematics, this is surely an error in the right direction. On the whole, the book fills the gap so long felt in thermodynamics, and the student on reading it should be able to follow with pleasure and profit the more advanced problems treated by the masters of the science.

J. S. A.

Corrections.

Vol. **24**, p. 49, line 13 *for* "$R.NH_3.\overset{\vee}{C}.CO$" *read* "$R.NH_3.O.\overset{\vee}{C}.CO$."

Vol. **24**, p. 276, line 2 from bottom, *for* "diamines" *read* "secondary amines".